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METALLURGY OF COPPER

USSR

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# FOREWORD

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METALLURGY OF COPPER  
USSR

Metallurgia Tsevetnykh Metallov  
/Metallurgy of Non-Ferrous Metals/,  
Moscow, 1957  
Pages 161-219,  
Russian, bk.

M. M. Lakernik  
N. N. Sevryukov

Chapter XIII

General Information

Copper, its tin alloys, called bronzes, and its zinc alloys, called brass, were known as far back as ancient time. Instruments, weapons, vessels, and decorations were made from copper and bronze. Because copper and brass have a high corrosion resistance they are used to coat the hulls of ships and as roofing material. Gun barrels, bells, and sculpture are cast from bronze which has better casting properties as compared to copper.

Copper is a better conductor of electricity and heat than iron and many other metals; therefore, with the development of electronics it has become the chief material for conductors, cables, busbars, contacts, and other current conducting parts of an electrical plant. The electronics industry consumes about 50% of all copper produced.

The high heat conductivity of copper determines its wide use in the manufacture of various types of heat exchangers: heaters, refrigerators, internal combustion engine radiators, and other similar devices.

Alloys of copper and zinc constitute the vast group of brasses, which include tombac (90% Cu and 10% Zn), Muntz metal (60% Cu, 30% Zn, tin and lead) and many other alloys, containing from 60 to 90% Cu. The mechanical stability of all brasses is higher than copper and so is its naturally good machinability by pressure and cutting, its high corrosion resistance, and considerable electrical conductivity. In addition to

this, brass is cheaper than pure copper since the zinc which is part of it is cheaper than copper. Brass is used in general in chemical machine building.

Alloys of copper and tin, called bronze, contains up to 20% Sn. Bronze is considerably harder than copper; however, it is well machined by cutting and has high casting properties. Its resistance to corrosion makes it possible to use bronze in the manufacture of reinforcements for water and gas pipelines and in the chemical industry, and its low friction coefficient -- in the manufacture of bearing bushes, worms and worm gears, reducing gears, and other parts.

Tin, a constituent of bronze, is more expensive than copper. In order to cheapen bronze and save the tin which is difficult to obtain, bronze, which has little or no tin, is used. To the former belongs, for example, bronze of the OTS and OTSS type, in which part of the tin is replaced by zinc and lead, and to the latter belong bronze, type BAZHM (aluminum, iron, manganese).

Besides bronze and brass, the assortment and fields of use have expanded considerably with the development of the industry and technology, and alloys of copper with other metals, for example, with nickel, as well as triplex and more complex alloys, have attained great importance in the rational economy.

Copper and nickel alloys are used in comparatively small amounts: the most important of them is German silver (80% Cu and 20% Ni) and Monel metal (68% Ni, 28% Cu, Silicon and iron). The exceptionally high resistance of Monel metal to corrosion, together with its high mechanical properties and easy machinability, makes it possible to use it to manufacture parts in exact machine building, surgical instruments and apparatus for fine chemical technology.

Copper salts, chiefly copper sulphate  $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ , is used in the chemical, leather, and fur industry, in dye works and in the production of artificial silk.

The average yearly production of copper in the main capitalistic countries per five years of the 19th and 20th centuries (thousands of tons) is listed below:

Years	1801- 1805	1826- 1830	1851- 1855	1876- 1880	1901- 1905	1926- 1930	1946- 1950	1952- 1955
Average Yearly Output	7.4	20.0	38.1	145.8	596.0	1603.0	2070.0	2375.0

In our country the copper smelting industry arose in ancient time; however, up until the XVIII century it was very minor.

The copper smelting industry began to produce at the beginning of the XVIII century in Russia, and the center was the Urals. In the middle of the XVIII century copper began to be smelted also in Altay, in the Caucasus, and in Western Siberia.

The government of the Czar did not aid the development of native metallurgy and transferred the large deposits of copper ore to foreign concessions. The smelting of copper in Russia sharply fell in the First World War, and by 1918 it just about ceased to exist.

The reconstruction and development of the copper industry during the first years of Soviet power was closely tied up the execution of Lenin's program of electrification, introduced at the IX Congress of the Party, and with the plan of GOELRO /State Commission for the Electrification of Russia/ which was based on this.

#### # 34. RAW MATERIAL FOR OBTAINING COPPER

The content of copper in ores rarely exceeds 1-5%. Rock, containing less than 0.3% copper, is not processed at the present time since it is not profitable in modern technology. Table 9 shows the most common copper minerals.

Table 9

#### Characteristics of the Most Important Copper Minerals.

Mineral	Chemical Formula	Copper Content %
Chalcopyrite (Copper pyrite)	$\text{CuFeS}_2$	34.6
Bornite	$\text{Cu}_3\text{FeS}_3$	55.6
Chalcocine	$\text{Cu}_2\text{S}$	79.9
Covellite	$\text{CuS}$	68.5
Malachite	$\text{CuCO}_3 \cdot \text{Cu(OH)}_2$	57.4
Azurite	$2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$	55.1
Cuprite	$\text{Cu}_2\text{O}$	88.8
Tenorite (Melaconite)	$\text{CuO}$	79.9
Chrysocolla	$\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$	36.2
Native Copper	$\text{Cu}$	up to 99.9

Solid pyrites, consisting chiefly of sulfides of copper and iron, and phenocrysts are among the sulfide copper ores. The latter are impregnations of sulfides in quartz and silicate rocks, and are sometimes microscopically thin. Pyrite ores are distinguished from the pyrites by a considerably higher content of sulphur and copper.

Oxidized ores are formed in nature as a result of the oxidation of sulfide ore minerals, primarily the impregnated type, and therefore, the chief iron admixture in them is in the form of oxides, carbonates and silicates.

Mixed copper ores are products of sulfide ores which have not been completely transformed into oxidized ore: Like oxidized ores they contain sulfide copper minerals.

Table 10

Composition of Copper Concentrates<sup>1</sup>

Raw Ore	Content %						
	Cu	Zn	S	Fe	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO
Cuprous pyrites	8-20	1-2	35-43	32-37	3-5	3-7	0.5-2
Copper zinc	8-15	2-4	30-35	25-30	3-5	3-7	0.5-2
Phenocrysts	20-25	-	30	25-27	5-10	5-8	0.5-2
Porphrites	28-35	-	15-20	16-20	20-29	5-8	1-2

<sup>1</sup>

N. N. Dnev, S. A. Vermenchev, A. S. Pen'ko. Reverberatory Smelting of Copper Ores and Concentrates, Metallurgizat [State Scientific and Technical Publishing House for Literature on Ferrous and Nonferrous Metallurgy], 1954, Page 27.

Copper ore sometimes contains other non-ferrous metals, especially zinc, lead, nickel, molybdenum, and frequently gold and silver, as well as sulphur, selenium, tellurium, thallium, and other rare elements.

The purpose of metallurgical reduction is the complex utilization of raw material and extraction, together with copper, of element impurities.

The physical characteristics of copper ore varies considerably. Solid pyrites are usually extracted from the interior of the earth in the form of fine grains of so-called bulk material [sypuchniki], oxidized ore is sometimes powdery.

The deposits of copper ore in foreign countries are concentrated chiefly in the American and African continents. The total copper resources here comprise 91% of the world's supply (excluding USSR); about 6% in a part of Europe, and about 3% in the deposit beds of Asia and Australia.

The largest copper deposits on the American continent are concentrated in Chili and the United States; in Africa--in Northern Rhodesia and the Belgian Congo; in Europe-- in Spain, Yugoslavia, and Scandinavia.

Copper concentrates, obtained as a result of dressing the ore by flotation means, contains from 8 to 35% Cu. In selective flotation of complex ores, lead, zinc, or nickel concentrates, which serve as raw material in the production of corresponding metals, must be separated, along with copper.

Obtaining rich copper concentrates is difficult chiefly because of the similarity of flotation properties of sulfide copper and iron minerals, as well as the close mutual intergrowth of these minerals in ores. Flotation is effected either by extracting the copper concentrate and pyrite residue, or by the method whereby a collective copper-pyrite concentrate is first obtained, and then separated by repeated flotation. 85-90% Cu is recovered from pyrite ores into a copper concentrate. Pyrite concentrate is a valuable raw material in the production of sulfuric acid; it contains about 45-50% S.

In the flotation of oxidized ores sodium sulfide is added to the pulp; therefore, the surface of copper minerals is covered with a film of copper sulfide.

Selective flotation will transform complex ores, for example, copper-zinc ores, into a copper concentrate 80-94% Cu, and a zinc concentrate 65-70% Zn.

Table 10 shows the composition of copper concentrates, and Table 11-- the material balance of flotation of copper sulfide ore.

Table 11

## Approximate Material Balance of Copper Ore Concentration

	Wt. m	Cu		Fe		S		SiO <sub>2</sub>		CuO		Al <sub>2</sub> O <sub>3</sub>	
		%	m	%	m	%	m	%	m	%	m	%	m
Loaded													
Ore	150	2.0	3.0	39.3	58.9	45.0	67.5	7.0	10.5	2.7	4.0	3.5	5.3
Received													
Concentrate	15	17.0	2.5	34.7	5.2	38.9	5.8	4.5	0.7	2.0	0.3	3.0	0.4
Tailings	135	0.4	0.5	39.8	53.7	45.8	61.7	7.3	9.8	2.6	3.7	3.6	4.9
Total	150	-	3.0	-	58.9	-	67.5	-	10.5	-	4.0	-	5.3

Extraction of copper into a concentrate:

$$E = \frac{2.5}{3.0} \cdot 100 = 83.3\%$$

Extraction of sulfur into residue:

$$E = \frac{61.7}{67.5} \cdot 100 = 91.4\%$$

Secondary raw material is debris and tailings of copper and its alloys, the collection and sorting of which is done according to the separate types. The tailings of various sorts of brass and bronze are treated separately, smelting them into alloys and correcting the composition with appropriate additives. Poor and so-called declassified tailings are those which can not be precisely classified; they usually contain from 8 to 75% Cu).

### # 35. METHODS FOR OBTAINING COPPER FROM ORE AND CONCENTRATES

Copper is extracted from ore and concentrates by smelting or leaching. The pyrometallurgical method is more suitable for the majority of types of raw material and, therefore, is more widespread throughout the world.

#### PYROMETALLURGICAL METHOD

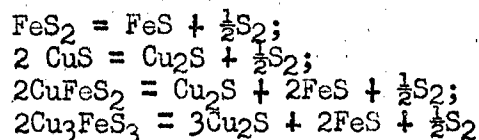


Minerals, amalgamated with ores, do not change their composition during concentration. There are only quantitative and not qualitative differences between the compositions of ore and concentrates, therefore, the treatment of ores and concentrates have one and the same physical-chemical basis.

If sulfide ore or the concentrate obtained from it is smelted, the smelted mass is divided into two liquid layers: an alloy of sulfides and an alloy of oxides. The different specific gravities and small mutual solubility of the smelted sulfides and oxides explains the scaling.

Sulfide alloys are called mattes, and oxide alloys--slag. Slag floats over matte since the specific gravity of matte is about 5, and the specific gravity of slag is about 3.

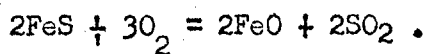
Even before smelting copper and iron minerals change their composition substantially, by decomposing with the formation of simple sulfides and sulfur vapors:



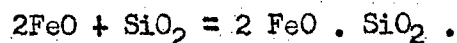
At the same time, simple iron and copper sulfides are stable at comparatively high temperatures; therefore, smelted matte, independent of the mineralogical form of copper and iron sulfides as raw material, will always be an alloy  $\text{Cu}_2\text{S}$  and  $\text{FeS}$ .

Barren rock ( $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ) changes during smelting into slag, which can easily be separated from matte and withdrawn from the process. Consequently, even simple smelting of ore or concentrate makes it possible to concentrate copper in matte.

In order to transform even part of the iron from sulfide into slag, it is necessary to oxidize it, for example, with oxygen from the air:



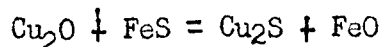
Iron is not oxidized up to  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  since there is a sufficient amount of quartz in the charge with which the ferrous oxide is combined in a stable silicate:



At the same time, it is possible to oxidize  $\text{Cu}_2\text{S}$ .



However, only FeS is actually oxidized, since Cu<sub>2</sub>O reacts with ferrous sulfide and is sulfidized:

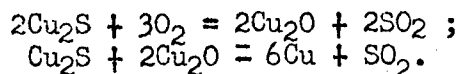


This reaction is a basic one in pyrometallurgy of copper. Because of the swiftness with which this reaction takes place, the copper remains in the form of sulfide and is concentrated in the matte, and the iron, to a considerable extent, becomes slag in the form of 2FeO . SiO<sub>2</sub>. Because of this, the content of copper in the matte grows.

The completeness of oxidation of ferrous sulfide during smelting is characterized by the degree of desulfurization (the degree of burning of the sulfur) is the ratio of the weight of sulfur to its weight as the initial raw material, expressed in percents or parts of a unit. The more that the iron and sulfur are oxidized, the richer the matte will be with copper.

Part of the sulfur can be oxidized before it is smelted by resisting, usually used for raw material with a high content of sulfur. If during roasting or smelting, all the sulfur, combined with iron, is oxidized, the iron is completely turned into slag. The matte obtained is close in composition to pure cuprous sulfide (79.9% Cu). Such matte is called white matte.

In order to obtain metallic copper, the smelted white matte is blown with air: the cuprous sulfide is oxidized at the same time to cuprous oxide, and the latter at the moment it is formed, reacts with the sulfide residue:



When the ore or concentrate is smelted it is not feasible to obtain the white matte directly since, with an increase of copper in the matte, mechanical losses of copper in slag grows because the fine grains of matte do not completely precipitate. At first it is better to obtain a relatively poor matte from the raw material and, consequently, a poor waste slag, which can be removed from the process. The iron residue from such a matte is discharged in the converter, which is similar to the Bessemer converter used in steel smelting.

When the matte is first blown in the converter the very same reactions take place as during ore smelting, resulting in the selective oxidation of iron from matte. Ferrous oxide forms slag with the addition of quartz in the converter.

After all the iron is oxidized and white matte is obtained, the converter slag is poured off and sent for a repeated processing since it is rich with copper.

The white matte continues to be blown with air, as a result of which metallic copper is obtained, called Rough; the rough copper is then refined--that is, cleaned of impurities.

In the past hundred years the matte is smelted directly from ore. With the modern development of ore flotation it is frequently enriched first of all, thus obtaining concentrates, which are then smelted. This greatly increased the total extraction of copper from ore and lowered its cost.

Nevertheless, direct smelting of ore is used at the present time; enriching the ore is profitable only when gold and silver turn into copper concentrate since, when the concentrate is smelted, these metals become copper and can be extracted from it by electrolytic refining; in case part of the precious metals become flotation tailings the necessity arises of giving the tailings an additional treatment, which is not always possible and feasible. A second circumstance, which sometimes causes a situation whereby ore can not be directly floated or treated, is the possibility of extracting incidentally elementary sulfur with copper from copper ore. Such a method has been developed, introduced into production, and has undoubted advantages, providing for the utilization of raw material.

In each separate case the treatment method is selected on the basis of technical and economic calculations, taking into account those considerations listed above adaptable for this or that deposit.

Figure 87 shows the general layout of copper pyrometallurgy; it includes direct smelting of ore, smelting of the concentrate after preliminary roasting and smelting of the concentrate without roasting. After inspecting it with application to sulfide ores and concentrates, we see that in order to separate the copper from iron it is necessary to oxidize and remove part of the sulfur with gases. The mixed copper ores contain less sulfur than the sulfide ores and, therefore, they can be treated by the very same method but at a lower degree of desulfurization. The oxidized ores can be smelted in mixtures with sulfides. Consequently, smelting to matte is suitable for any raw material provided that the sulfur in it is sufficient to form matte.

The raw and heated copper concentrates are powdery; therefore, reverberatory or electric furnaces, suitable for smelting fine charges, are used for smelting them into matte.

Copper ores are usually lumpy, and only shaft furnaces are suitable for smelting, as a rule. Sometimes the concentrates become briquets or form clinkers, and then they are smelted in shaft furnaces; fines are loaded along with concentrates into the reverberatory or electric furnaces.

### COPPER MATTE

Matte is an intermediate product when copper is obtained from ore and concentrates. The cost of smelting copper depends, to a great extent, on the composition and properties of matte.

In addition to our first statement about mattes, that they are alloys  $\text{Cu}_2\text{S}$  and  $\text{FeS}$ , we must note that in practice that in the matte the total content  $\text{Cu}_2\text{S}$  and  $\text{FeS}$  rarely exceeds 80-90%; sulfides of zinc, lead, nickel and other impurities comprise the residue up to 100%, as well as oxides of iron, silicon, aluminum, calcium; that is, the components of slag which are partially soluble in matte. Ferrous oxides as compared to other oxides are quite soluble in matte; the other oxides are comparatively not very soluble in matte. Liquid mattes dissolve precious metals very well; because of this, and the fact that they are not very soluble in matte, gold and silver become mattes when copper is smelted.

The maximum possible content of copper in matte is 79.9%. Mattes, which contain less than 10% copper, are avoided, if possible, because it is both difficult and expensive to process them.

Usually matte contains 30-40% Cu.

There is 36.4% in ferrous sulfide, and almost 20% S in cuprous sulfide. It is understandable that the content of sulfur in mattes must lie within these limits, and it is usually 24-26%. On the basis of this, Professor V. Ya. Mostovich made the rule that under metallurgical calculations the content of sulfur in any copper matte is 25%.

Investigating the mattes, Professor V. Ya. Mostovich established that they contain oxygen, which is a part of the ferrites which are soluble in matte; that is, in compounds like  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ . The oxygen in matte is usually 7%; the content of it is higher, the poorer the matte is in copper.

The smelting temperature and the specific gravity of matte are important properties and depend on the composition. Rich mattes have a high specific gravity and the more refractory they are, the poorer they are. Factory mattes are smelted at 900-1150° and have specific gravities at about 4.6-5.7.

## SLAGS FROM COPPER SMELTING

Slag from copper smelting is in a majority of cases, a waste product. The yield of slag is sufficiently great: for each weight unit of smelted matte there are up to 10 units of slag when the content of Cu in it is about 0.1-0.5%. If the content of copper in matte is 50%, it is not difficult to estimate that the slag removed is 10% of all the metal. The economics of copper smelting depends to a great extent on the yield of slag and the content of copper in it.

The yield of slag is determined by the composition of the processed raw material and the quantity of added fluxes. The content of copper in slag depends on the composition of slag and the smelting conditions.

The following are the various types of copper losses in slag:

1) CHEMICAL, due to an incomplete reaction between  $\text{Cu}_2\text{O}$  and  $\text{FeS}$ ; therefore, part of the copper remains in the slag as dissolved  $\text{Cu}_2\text{O}$ . As the research of V. A. Vanyukov and other scientists indicated, these losses are not great and there is no essential importance;

2) PHYSICAL, the diffusion of  $\text{Cu}_2\text{S}$  in slag; the solubility of sulfides depends on the composition of slag and on temperature: however, at the maximum it does not exceed 0.2-0.3%;

3) MECHANICAL, as a result of incomplete precipitation of drops of matte because of the small difference in the specific gravities of matte and slag, the high viscosity of the slag, and the short duration of precipitation etc, these losses are very important.

The composition of the raw material must be selected so that the most viscous and the lightest slag is obtained. In addition to this, it is necessary to try to use the minimum amount of the cheapest fluxes.

Slags from copper smelting, in the majority of cases, are similar to the slags from nickel, lead, and tin smelting, and the chief components are:  $\text{SiO}_2$ ,  $\text{FeO}$ ,  $\text{CaO}$ ; the total content of these components reaches 80-90%. Moreover, slags contain up to 15%  $\text{Al}_2\text{O}_3$  and in some cases up to 25%  $\text{Fe}_3\text{O}_4$  (converter slags), as well as oxides of magnesium, barium, sodium, and other metals.

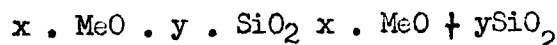
The smelting temperature of slag must correspond to the process conditions: too many high melting slags raise the price of smelting, causing an increase in the cost of fuel and deterioration of the refractory material. Slags from copper smelting are usually smelted at 1050-1200°.

Separate components of slags have very high smelting temperatures, for example,  $\text{SiO}_2$ -1680°,  $\text{FeO}$ -1320°,  $\text{CaO}$ -2570°. Their various combinations are smelted at much lower temperatures because of the formation of easily smelted mixtures and chemical compounds.

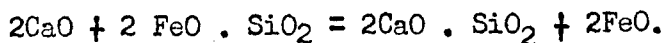
Slags belong to substances of the vitreous type which do not have a smelting point. At a definite temperature interval they gradually go from a hard state to a liquid one; therefore, for a complete statement concerning the fusibility of slags one must be guided not only by the smelting temperature, but by viscosity.

Increasing the content of  $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{CaO}$ ,  $\text{BaO}$  in slags is accompanied by a decrease in viscosity;  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{Fe}_3\text{O}_4$  and certain other oxides increase the viscosity of slags. In a number of cases substances which are not easily soluble in slags increase the viscosity, becoming slags in the form of hard particles, suspended in a liquid fusion.

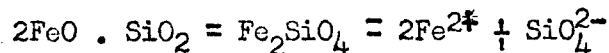
The oxides, which comprise slag, form chemical compounds, chiefly silicates of the type  $x\text{MeO} \cdot y\text{SiO}_2$ . According to the widespread ideas concerning the nature of slags, chemical compounds in them break down into free oxides:



The degree of dissociation of the various silicates is not the same and depends on the stability of the tie between oxides, temperature, and concentrations in the liquid slag. Oxides, which form the most stable silicates, destroys silicates which are less stable, for example:



According to new ideas, which were first pronounced by Professor V. A. Vanyukov and, at the present time, are being developed by many scientists, the silicates in slag break down like salts:



The ionic electrical conductivity of liquid slag and the possibility of electrolysis by removing metal at the cathode has been confirmed by experience.

The specific gravities of slags depends on the composition. Factory slags from copper smelting have a specific gravity around 3.2-4.0. The oxides of iron, Manganese, and barium make slags heavy, and oxides of aluminum, silicon, magnesium, and calcium make them lighter.

## # 36. SMELTING MATTE FROM ORE

In order to extract a sufficiently rich matte from copper ore, which usually contains 1-2% copper, it is necessary to convert almost all the iron into slag, and to do this, it is necessary to oxidize the sulfur combined with it during the smelting process; that is, to have a high degree of sulfurization.

### PYRITIC AND SEMIPYRITIC SMELTING

The furnace for smelting copper ores is a high shaft, filled with a mixture of lumped ore, fluxes, and coke. Air is blown through the tuyers in the lower part. This is necessary to burn the fuel and oxidize the sulfides.

The furnace walls mesh with the smelted slag containing ferrous oxide. Refractory material, consisting of aluminosilicates or quartz, are not resistant to the action of such slags, and the magnesite brick does not have sufficient thermal and mechanical stability. Therefore, the walls of the furnace for copper smelting are made from caissons -- flat iron boxes, cooled by circling water in them. A layer of fused materials, which forms a crust on the exposed surface of the furnace, serves as the refractory material for this.

A rectangular iron slab, fastened to steel columns or jacks in the foundation, is the base of the furnace.

The caissons are welded from sheets of boiler iron (Fig. 88). The length of the caisson is from 1.8 to 5.5 m [meters], the width 0.6-1.5m, the thickness 120-150 mm. The thickness of the inner wall of the caisson is 10-20 mm [millimeters] and the outside wall 6-10 mm.

The caisson part of the furnace has in its cross section the form of a trapezium exposed to the small base below. The front caissons are vertical; each of them have a rectangular trapezium form. At the ends there are two caissons each.

The tyuere openings are placed along the long sides of the furnace. The tyueres, fastened to the caissons, are connected with an airpipe which feeds the blast.

Cooling water is fed to the outlet of each caisson from the main water pipeline. Warm water (70-80°), leaving the caisson, pours off into collecting troughs. In order to avoid the formation of scale, circulating water is constantly fed to the caissons. For this purpose warm water is cooled in cooling towers.

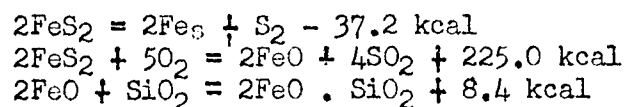
Matte and slag are discharged together through one opening in the long side of the furnace. At the outlet the caisson which forms a wall of the furnace, is shorter than the others; below it is a special outlet caisson which is a copper slab with flat coil attached to it. In the outlet caisson is an opening to which is joined a short and deep channel with cool water and lined inside with refractory brick. A baffle plate at the overflow end is higher than the outlet opening and, as a result, a hydraulic device is created from the layer of flowing smelted mass. The smelted mixture of matte and slag flows with a continuous stream into a settling tank placed in front of the furnace and called the front hearth (Figure 89).

The front hearth in the plan usually has the shape of an oval, its long axis perpendicular to the long axis of the furnace. It is lined with chrome magnesite or magnesite in a shell made of sheet iron. The top of the hearth is not covered, the crust of hardened slag serving as the crown. The matte and slag are scaled when they arrive in the front hearth. The slag is discharged along a channel at the end of the hearth opposite to the spot where the smelted mass enters. The matte is discharged periodically (as it accumulates) through a tap hole placed in the side walls at the level of the well of the hearth.

The gases go off through the tent [shater] chamber made of chamotte brick which covers the furnace over the charging platform. Windows are built in the side walls of the tent for charging, which are closed by hinged suspended doors. Iron gas-pipelines, lined inside with refractory brick pass through the crown of the tent. Through these gas pipes the gases go into a settling chamber so that the dust can be collected.

The process of shaft smelting of copper ore is characterized by the fact that the basic heat, necessary for smelting, is obtained from the oxidation of the components of the ore -- pyrite and other sulfides -- as well as the formation of silicates of ferrous oxide and calcium oxide.

The formation of iron oxide silicate from pyrite takes place in the following way.



Computation indicates that when the ore contains no less than 37% S (69.4%  $\text{FeS}_2$ ) smelting is possible without the use of additional fuel.



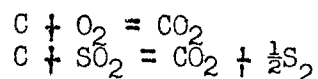
Under production conditions smelting is possible without the use of fuel is very unstable; therefore, no less than 2% coke is always added to the ore. However, the chief amount of fuel is obtained from the oxidation of pyrite, and such smelting is called pyritic. Increasing coke consumption helps to stabilize the process and ease the regulation of it. Smelting with the addition of more than 6% coke is called semipyritic.

Large-scale research in the field of theory and thermal chemistry of pyrite and semipyritic smelting belongs to academician A. A. Baykov and Professor V. Ya. Mostovich.

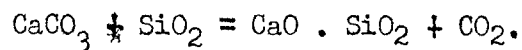
When copper ore is smelted in shaft furnaces pyrite and coke burn most strongly around the tuyeres": the temperature here reaches 1400-1500°. Hot gases, penetrating the load [syp] height is 3-5 meters, rise and leave through the tent to the dust catchers, and then they are either utilized (use of sulfur dioxide), or they are thrown back into the air through the smoke pipe. The temperature of gases at the level of the charge hole is 350-550°.

The lower layers of the load are smelted; settling, the charge gradually descends to meet the stream of hot gases, and the temperature gradually rises.

As the temperature rises the dissociation of the higher sulfides - pyrite, chalcopyrite, covellite and bornite - completes itself; sulfur fumes leave as gases, oxidizing in passing until they become  $\text{SO}_2$  and  $\text{SO}_3$ . Then the sulfides ignite, their speed of combustion grows with the temperature. The carbon of coke oxidizes with oxygen and sulfur dioxide:

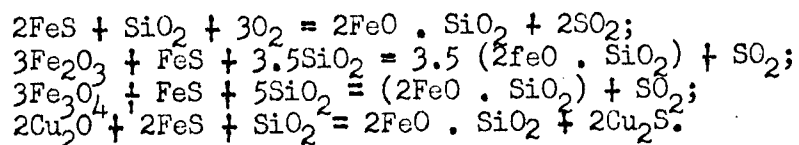


When there is little expenditure of coke (approximately 2%) the coke carbon burns for the most part in a second reaction in the upper parts of the furnace. Limestone dissociates into  $\text{CaO}$  and  $\text{CO}_2$ . When limestone comes into contact with silicon dioxide the speed of this reaction increases considerably:



When temperatures are about 1000° sulfides begin to smelt out from lumps of ore, leaving behind a porous shell of quartz, and oxides of iron, calcium, magnesium, and aluminum. The most easily fusible alloys in the system  $\text{SiO}_2 - \text{CaO} - \text{FeO}$  are smelted at 1030°; flowing downward they gradually dissolve in themselves other oxides of gangue.

The porous mass of hard oxides, which were formed as a result of smelting easily fusible components, plays an important role in the smelting process. In the pores of this mass the smelted stream of sulfides meet the incoming stream of hot oxygen-containing gases. Due to the large surface of contact and high intensive temperature the most important reactions of smelting take place:



The smelted mixture of sulfides and silicates flow downward and are discharged in order to settle in the front hearth.

The degree of combustion of sulfur, when copper ore is smelted in a shaft furnace, depends on the conditions and behavior pattern of the process and constitutes 50-95%. Thanks to such a high degree of desulfurization rich matte can be obtained from poor ore.

If coke is added in small amounts, it burns in the upper horizons of the load for the most part from  $\text{SO}_2$ , not reaching the area of the tuyeres (pyrite smelting). When there is a large consumption of coke, air oxygen, blown thorough the tuyeres, is expended in burning it. As a consequence of this, the degree of combustion of sulfur during smelting is lowered. At the very same time, burning coke in the area of the tuyeres creates a more stable heat condition in the focal point of burning; such a situation is characteristic of semipyrritic smelting.

Slag from shaft smelting basically contains  $\text{SiO}_2$ ,  $\text{FeO}$  and  $\text{CaO}$  (Cf. table 12).

Selection of the ratio of these components in the slag received is closely tied up with smelting conditions and especially with the consumption of fuel -- coke. When there is little consumption of coke and the ore consists chiefly of pyrite, only quartz can be added as a flux. Additions of limestone and other materials in the charge must be at a minimum; otherwise, the heat from burning the pyrite will not be sufficient to smelt the charge.

Table 12

EXAMPLES OF THE COMPOSITION OF SLAG FROM SHAFT  
SMELTING OF COPPER ORE

Method of Smelting	Composition of Slag, %							
	Cu	SiO <sub>2</sub>	FeO	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	S	ZnO
Pyrite	0.18	32.6	49.9	8.2	1.5	3.5	1.7	1.9
"	0.15	32.5	52.2	4.8	7.2	-	0.9	-
Semipyrritic	0.16	30.0	34.6	12.0	11.0	-	-	-
"	0.16	39.9	22.4	26.8	6.4	-	0.5	1.4
Copper-sulfur	0.20	33.6	52.8	6.0	1.6	-	2.9	0.6
"	0.18	32.4	55.2	6.0	-	-	-	trace

Slags from pyrite smelting are close in content to the iron oxide silicate  $2\text{Fe} \cdot \text{SiO}_2$ . The content of calcium oxide, introduced in order to lower the melting temperature and the specific gravity of the slag, does not exceed 5-6%. Slags from pyrite smelting frequently have a high viscosity because of the presence of suspended particles of magnetite in them. The formation of magnetite is a consequence of the destruction of the direct contact between quartz and iron sulfide when the latter is oxidized. Iron sulfide is oxidized moreover to  $\text{Fe}_3\text{O}_4$ , which forms a suspension in the slag.

During semipyrritic smelting an additional amount of heat makes it possible for the slag to change its composition more freely primarily by decreasing the content of FeO, and this, in turn, helps to lower the specific gravity of the slag. In addition to this, the content of  $\text{SiO}_2$  in slags reaches 40-45%, and the content of calcium oxide 12-27%.

The coarseness of the ore, fluxes, and coke, which are charged into shaft furnaces, must be no lower than 20-15 mm millimeters when for the most part there are lumps whose diameter is about 100 mm. In order to avoid any significant decrease in the gas permeability of the pillar of the load the content of fines in the charge, represented as particles less than 20 mm, must not exceed 10%.

The charge portion, consisting of ore, fluxes and other materials (for example, reverse), intended for charging, is called a charge. The shaft charges are loaded according to a set graph and alternate with fuel charges of coke.

The matte from the front hearth is discharged periodically, according to its accumulation, and the slag flows continuously into slag buckets, hauled away to the dump, but sometimes it is granulated.

In order to preserve the established regime of blowing, the tuyeres must be periodically cleaned, a constant height of the load must be maintained as well as the coarseness of the charge.

With the passage of time the walls of the furnace on the inner surface form crusts, which sometimes reach such proportions that they almost cover a section of the furnace. There are various reasons for the formation of crusts, but the main one is the uneven distribution of the gas stream along the area horizontal to the section of charge, and this, in turn, causes the charge to be unevenly heated.

When there is a small amount of coke in the charge the stoichiometric ratio between the quartz, ferrous sulfide and oxygen from the air at various points of the smelting zone is destroyed, resulting in the formation of crusts. As a result of an excess of quartz or a deficient amount of air, during which  $\text{FeO}$  is not formed in the amount necessary to slake quartz, easily fusible silicate crusts are formed. When there is an excess of air or a deficient supply of  $\text{SiO}_2$ ,  $\text{FeO}$  is frequently oxidized to  $\text{Fe}_3\text{O}_4$  -- easily fusible magnetite crusts are formed.

When the consumption of coke is increased, the danger of forming crusts is less; however, in addition to this, it is necessary to systematically observe the condition of the profile of the furnace.

There are various ways to remove the crust, but it is always difficult; therefore, even pure pyritic ore is frequently smelted at an increased expenditure of coke.

An original method in the struggle against crust has been developed in our factories in the Urals, which operate with little expenditure of coke. Once a day charging is stopped for 1-2 hours, a so-called warming charge made up of ore with 10% coke is loaded into the furnace and covers the tuyeres that are covered with crust. After a certain length of time the crust is melted, and the remainder is knocked down with sharp rails.

Dust formation during shaft smelting reached 2-8% of the weight of the charge and depends on the amount of fines in it. The dust settles in the gas lines and the settling dust chamber, and the finer particles are caught with an electric filter. The composition of dust is usually close to the content of the ore. Most frequently the dust is treated in reverberatory furnaces along with copper concentrates, and is sometimes briquetted or forms clinkers and is smelted in shaft furnaces.

The main technical and economic indices of shaft smelting are the recovery of copper as matte, fusing, and expenditure of coke. The recovery of copper as matte during shaft smelting is 78-85%. Such comparatively low recovery is explained by the large yield of slag per unit of weight of the matte. The daily melting of the charge carries away about 1 m<sup>2</sup> of the furnace around the tuyeres; it varies from 60-130 t/m<sup>2</sup> per day. When there is little expenditure of coke the melting is lower; for example, with 2-3% of the weight of the coke it does not exceed 70 t/m<sup>2</sup>. When smelting is done according to the Urals method the outstanding workers of production will succeed in smelting 110-120 t/m<sup>2</sup> per day, expending on an average a total of about 3-3.5% coke.

The content of copper in mattes from shaft smelting depends on the content of the ore and the degree of combustion of the sulfur; it usually varies from 15-25%, although in some cases mattes with 45-50% Cu are obtained from rich ores.

The run of the shaft furnace is from 4 months to 1.5 years in an average 10-12 months.

#### COPPER-SULFUR SMELTING

Such is the name of the process of smelting copper ore, which obtains elementary sulfur in passing with matte; it was introduced into production abroad during the twenties, and in our country in the thirties.

The copper-sulfur smelting differs from methods of shaft smelting, which was developed earlier, by a larger expenditure of coke which permits a reduction atmosphere in the upper reaches of the shaft. In its lower reaches the atmosphere remains oxidizing. This is achieved by, besides an increased expenditure of coke, the hermetization of the charge hole and the loading device of the furnace.

The furnace walls for copper-sulfur smelting, as distinct from the walls of shaft furnaces for pyritic and semipyrritic smelting, are caissoned only in the lower part at a height of about 2.5 m. The surface of the caissons, which is faced toward the furnace, is lined with a thin layer of refractory brick; the upper part of the shaft is lined with chamotte brick and is enclosed in an iron shell for hermetization. The brick shaft is covered by an arched crown.

The charge is loaded through a hermetically sealed funnels, similar to the loading device of blast furnaces (Figure 90).

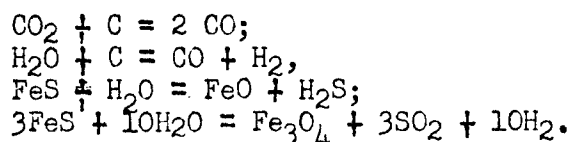
The outgoing gases are discharged through an opening in the longitudinal wall of the shaft near the crown.

The tapping hole for the slag and matte is placed over the level of the well which is higher than in the usual shaft furnaces, and the smelted products of the smelting inside the furnace are at a height of about 1 m over the very same level.

The smelted mass is discharged into the front hearth. The copper-sulfur smelting process is characterized by the already known chemical reactions such as heating sulfides to form oxides, reaction between cuprous oxide and ferrous oxide, and the formation of silicate of ferrous oxide.

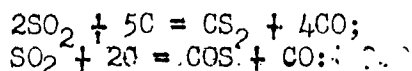
Coke carbon burns to  $\text{CO}_2$ .

Gases, containing  $\text{SO}_2$ ,  $\text{CO}_2$ , and an excess of oxygen and nitrogen, rise, penetrating the load; the excess of oxygen gradually is used up in the oxidation of sulfides and carbon. Carbonic acid, reacting with carbon, is partially changed into  $\text{CO}$ ; water, introduced by blowing and the charge, is either decomposed by coke carbon, or reacts with the sulfides to form hydrogen sulfide:

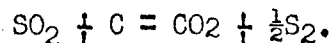


Thus, the composition of the gas changes as it moves upwards: the content of  $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{H}_2\text{O}$  decreases in it because of the formation of carbon oxide, sulfur dioxide and carbon oxysulfide.

At a high temperature sulfur dioxide is reduced by coke carbon forming carbon bisulfide:



in the upper levels of the load it is primarily elementary sulfur:



In the upper levels of the load the fumes of elementary sulfur, obtained as a result of the dissociation of pyrite, chalcopyrite and other higher sulfides, become gases.

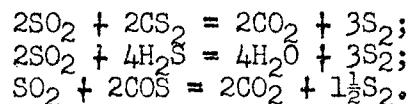
Waste gases have approximately the following composition ( $\text{g/m}^3$ ):

S <sub>2</sub>	SO <sub>2</sub> + H <sub>2</sub> S	COS	CS <sub>2</sub>	Dust
200-220	30-35	4.5-5.0	8.2-16	15-50

Gases must leave the furnace at a comparatively high temperature (420-450°) in order that they can be cleaned from dust before condensation of sulfur vapors takes place. The gases are discharged into the gas collector, assuring intermixing and uniformity in the composition of the gas. The basic mass of the largest sized dust settles in the gas collectors and gas lines, and the final cleansing of the gases of dust takes place in electric filters. The gas treatment diagram is shown in Figure 91.

The cleaned gas is fed into contact chambers, filled with a porous mass of catalyst, consisting of aluminum cement and aluminum hydroxide.

In the presence of a catalyzer at a temperature about 420°, reactions take place between the components of the gas mixture forming elementary sulfur fumes:



Gases from the contact chambers go to water pipe boilers. The sulfur is condensed in pipes and drains into a collector; heat, given off when the sulfur is condensed, is used to heat the water in the boilers. During condensation gases are cooled to approximately 120°. Sprinkling towers are used to catch the fine droplets of sulfur suspended in the gas. The gas is fed into towers toward the smelted sulfur flowing off along the checkered brickwork.

Only part of the sulfur will be extracted in the contact chamber and sprinkling towers; therefore, the gas, cooled to 120°, is again heated to 300° and sent to a second analogous system of apparatus, consisting of a contact chamber and condenser for the sulfur fumes, which catches the fine dust of the hard sulfur.

In order to render the spent gases harmless before they are discharged into the atmosphere they are sent through a tower with limestone which sprays them with water.

Mattes from copper-sulfur smelting contain 8-15% Cu. In order to facilitate subsequent extraction of copper, mattes undergo a process called concentration smelting. This smelting is carried out in shaft furnaces of the same type as described above; the outgoing gases of these furnaces are usually not converted into sulfur since the content of sulfur compounds in them is comparatively low; but sometimes they are used in the production of sulfuric acid. The degree of burning during

concentration smelting reaches a total of only 30-50%, since matte does not contain the higher sulfides.

Mattes are loaded into the shaft furnaces in the form of lumps 30-100 mm large along with quartz, limestone, and coke. The expenditure of coke comprises 7-8% of the weight of the charge.

Concentration smelting is similar in its chemical activity to ore smelting. As a result of this concentration smelting, matte rich in copper, containing 25-40% Cu, and slag with 0.4-0.8% Cu, are obtained.

The technical and economical indices for the smelting of a charge from copper-sulfur smelting is lower than for smelting with open charge holes: smelting comprises a total of about 35-45 t/m<sup>2</sup> or the section surrounding the tuyeres: the consumption of coke is considerably higher, approximately 7.5-10% of the weight of the charge.

The balance of sulfur in the copper-sulfur smelting process is approximately the following (%):

Extracted as elementary sulfur.....	68
Changed to matte.....	10
Lost in slag.....	5
Lost in spent gases.....	17

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Total.....	100
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### # 37. EXTRACTION OF MATTE FROM CONCENTRATES

Copper concentrates are powdery; they consist chiefly of particles 0.05-0.1 mm large. Such a fine material lies as a thick layer and it is difficult for air to reach the inside, and, therefore, it is difficult to smelt the required amount of sulfur during the smelting. In order to obtain the necessary degree of desulfurization the concentrate is roasted before it is smelted in multihearth mechanical furnaces or in a burning layer, as described in chapter VIII. However, if the sulfur in the concentrate is low, or if there is the possibility of smelting the sulfide concentrates in a mixture with concentrates from oxidized or blended ore, roasting is unnecessary. In that or any other case where the hot components in the charge are less than in shaft smelting, the heat of the chemical reactions is far from sufficient for smelting, and consequently fuel is necessary for smelting concentrates.



The concentrates are smelted in reverberatory or electric furnaces. Electrosmelting has a number of advantages over reverberatory smelting which will be described below; however, under ordinary conditions it is more expensive than reverberatory smelting because of the high expenditure of power. Under modern conditions reverberatory furnaces are chiefly used, but in regions where electric power is cheap or there is no fuel, suitable for reverberatory furnaces, electric smelting is used.

### SMELTING IN REVERBERATORY FURNACES

The reverberatory furnace for smelting copper concentrates, shown in Figure 92, is a tunnel-shaped chamber made of refractory brick, laid out on a foundation of solidified slag. For the foundation arrangement a trench is dug and lined with a form of rubblestone and concrete corresponding to the measurements of the furnace. This form is then filled with smelted slag.

The walls of the furnace are lined with Dinas brick 2-1 $\frac{1}{4}$  bricks thick; that is, 500-565 mm. In order to preserve the lower part of the walls from reacting with the smelted products a lining of magnesite or chromomagnesite is used at a height of about 1.5 m. For the same purpose some factories cool the outside surface of the walls with water (the water flows along coils, poured into cast iron sheets.)

The crowns of reverberatory furnaces are arched (Figure 93) and suspended (cf. diagram in Figure 94). The arched crown is about 500 mm. and is lined with wedge-shaped Dinas brick, which resists contraction at high temperatures better than other refractory material. However, the Dinas brick has less chemical stability under reverberatory smelting conditions than other neutral refractories. The strength of a Dinas brick crown limits the width of the furnaces. The various parts of the crown do not wear out alike, and partial repair of arched crowns is difficult. Suspended crowns were used starting in 1931 with magnesite and chromomagnesite brick as the material for them. Dinas brick crowns are suitable for an acid charge, and magnesite for a base charge.

Double T-beams or riveted steel columns are set in pairs at intervals of 0.9-1.8 m along the wall in order to strengthen the furnace. Opposite pairs of beams are drawn together by connecting rods which pass over the crown. When the furnace is heated the nuts of the rod gradually loosen.

Preparing the surface of the sole of the reverberatory furnace, called the well, is a very important operation: to do this, a layer of refractory clay 50-100 mm thick is first tamped on a brick layer, which lines the slag foundation, and then, a layer of pure quartz sand 600-700 mm thick. When it is heated to 1500-1600° the quartz becomes tridymite (another crystalline modification of quartz), and separate grains are welded, forming a dense, smooth surface.

Coal dust is blown into the furnace by gas burners, and mazut by oil burners through openings in the front face wall. Usually the gas and oil burners (4-6 pieces) are placed in one row. The air for blowing or spraying is supplied by a ventilator at a pressure of 200-250 mm water column [вод. ст.] and is called the primary air, and an additional amount of "secondary" air is blown through openings along side the oil burners (gas burners).

The calorific value of coal dust is less than that of mazut; its defect is its comparatively high ash content. The materials are heated in reverberatory furnaces with an open flame; the ash falls to the surface of the smelted bath and can have an effect on the composition of the products of smelting or, if it is highly fusible, can worsen the conditions of transferring the heat from the gases to the bath. The calorific value of coal must be no less than 6060 kcal/kg, the ash content--no more than 15%, the content of volatiles--about 25%. With all its defects coal is cheaper and easier to obtain than mazut; therefore, it is used in the majority of copper smelting plants.

The temperature of the gases in the furnace has the highest value in a distance of about 3.5 m from the front wall, reaching 1550-1600°. At half the length of the furnace the temperature is reduced to 1300-1350°, and in the tail end 1250-1200°.

The heat efficiency of reverberatory furnaces is very low, no more than 30%, because of the high temperatures of the waste gases. In order to increase the degree of utilization of fuel the waste gases go to steam kettles, and then, the heat utilization coefficient increases to 55-65%.

The charge is loaded through openings in the crown, placed near the furnace, along the side walls. Bunker chutes, situated in the charging platform over the furnace, are lowered into the charging openings. The charge is fed into the bunkers by carts or conveyor belts. The loaded charge lies at an angle along the walls, preserving the floor from any direct action of the slag and hot gases.

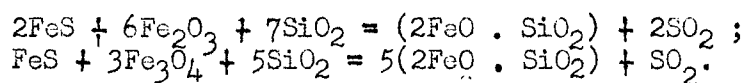
Liquid converter slag is poured into channels, the end of which leads into the furnace into the front part of one of the side walls or through a window in the front face wall.

The products of smelting--matte and slag--are discharged as they accumulate. Slag is discharged through a slag window in the back part of the furnace (in the side or face wall) 700-800 mm above the well; the necessary level of slag is maintained by a little embankment of refractory clay. There are usually two openings for discharging the matte and they are at the level of the well in one of the side walls (rarely in the front face wall). A water cooled cast iron or copper slab with square holes, in which are inserted cast iron bushes (tapping holes) with an internal diameter of 45-50 mm, are laid at the spot where the matte is discharged into the wall of the furnace.

The control regulation of the heat conditions in reverberatory furnaces are automatic in the majority of modern plants. On the basis of automatic measurements of the temperature, the amount of fuel, air, and draft is maintained at a set smelting regime.

#### SMELTING RAW (NOT ROASTED) CONCENTRATES

The charge, comprised of the concentrate and fluxes, is carefully agitated in mechanical mixers or disintegrators. The homogeneity of the charge ensures its timely smelting and the swift flow of the necessary chemical reactions during the smelting process. Loading is carried on either continuously or periodically according to the chart. The dissociation of higher sulfides begins forming  $\text{FeS}$  and  $\text{Cu}_2\text{S}$  as the charge is heated, then the mixtures of these substances are smelted giving the primary matte. The liquid matte flows along slopes into a bath, reacting in passing with the hard components of the charge, chiefly with iron and quartz oxides:



Copper sulfide can also be oxidized by iron oxides or the oxygen  $\text{O}$  from the furnace gases, but, reacting with ferrous sulfide it is again sulfidized according to the basic reaction of copper pyrometallurgy, that is,:



As a result of this, the matte flowing into the bath is enriched with copper and becomes poor in iron. Its final composition is established in the bath where the very same reactions take place at the separation border of matte and slag.

The direct oxidation of sulfides with oxygen from the furnace gases in reverberatory smelting takes place to an exceedingly small degree because of the small content of oxygen in the gases and the difficulty of diffusing it inside the layer of the charge that lies snugly at an incline; the iron oxides in an unroasted charge is also small. The chief mass of sulfur is removed because of the dissociation of the higher sulfides; the total degree of desulfurization does not exceed 50%, therefore, poor mattes, diluted with ferrous sulfide, are obtained from highly sulfurous concentrates.

Precious metals--gold and silver-- are extremely solvent in liquid mattes; their solubility in slags is insignificantly small, therefore, it is feasible to use rock, containing gold and silver, for example, poor gold ore, concentrates of gold ore and other similar materials, as fluxes in reverberatory smelting, especially if the direct extraction of gold from them is difficult.

#### SMELTING OF ROASTED CONCENTRATES

The smelting of roasted concentrates does not differ from that described for raw concentrates, but it does have its own physical and chemical peculiarities.

The charge for smelting is prepared before roasting so that it may be carefully mixed while it is in the roasting oven and also so that the fluxes from the heat of the roasting oven may be dried and heated. Loading the dry hot charge into the reverberatory furnace increases the smelting and lowers the expenditure of fuel during the smelting process.

The purpose of roasting is to remove part of the sulfur which is necessary in order to obtain rich matte. The chemical activity of the roasting and its methods of behavior were described in chapter VIII. At the present time a majority of plants roast the copper concentrates in multihearth mechanical furnaces, which are complex in construction, tremendous and produce very little. In one cubic meter of the volume of a standard furnace of this type 150-170 kg, of sulfur are burned every 24 hours and the spent gases contain no more than 7%, and usually 4.5-6%  $\text{SO}_2$ . More perfected and productive furnaces for roasting in the boiling layer have already been set up in some copper smelting plants. They have succeeded in roasting 750 kg of sulfur every 24 hours under this very same degree of desulfurization in one cubic meter of the furnace area; that is, the content of  $\text{SO}_2$  in the waste gases will reach 12-14%.

As a result of roasting, the content of sulfides decreases considerably, and the content of iron oxide --  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  -- grows. The temperature of the hot roasted charge is 450-500°. For ease in loading the hot charge, the roasting ovens are sometimes placed over the reverberatory furnaces.

When the roasted charge is smelted the reactions between the oxides and sulfides of iron become extremely important:  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$  and ferrites must be completely reduced since all these substances are not very soluble in slag. When they are converted into slag as suspended hard particles, they make it heavy and viscous, hard to separate from matte. The reduction reactions of ferrous oxides were discussed earlier in the description of the smelting of raw concentrates. The ferrites are also reduced in a similar reaction. Frequently the reduction of ferrites does not finish in slopes and continues in the bath just on the border of separation of matte and slag. Droplets of sulfur dioxide separated moreover, attract particles, of matte in a slag layer, as a result of which slag from smelting a roasted charge carries away more unstable matte than that carried away in the smelting of raw concentrates; the extraction of copper as matte is lower.

Copper becomes matte as a result of those same reactions as in the smelting of a raw charge; its oxide is reduced by ferrous sulfide, and then is sulfurized:



When a roasted charge is smelted there is less desulfurization than when a raw charge is smelted since the sulfur of the higher sulfides are removed during roasting. A small amount of sulfur (about 20-40%) burns chiefly because of the reactions between the ferrous oxides and ferrous sulfide.

#### SLAG FROM REVERBERATORY SMELTING

Slag is discharged periodically through a slag window and to do this the little embankment of refractory clay which maintains the level of slag is destroyed. The slag, flowing along the channel into the slag bucket, is carted off to the dump; it is frequently granulated when it is discharged from the furnace. The granulated slag is used in construction and for filling mine workings. It is sometimes poured in the form of slabs and used in road construction or for other construction purposes.

The yield of slag in reverberatory smelting exceeds the yield of matte by weight 2-3 times and 3-5 times by volume. Consequently, its effect on the technological and economic indices for conversion is great. In evaluating the losses of copper in slag it is necessary to pay attention not only to its percentage content but also to the yield of slag.

The reactions between the ferrites and ferrous sulfide are not completed until the beginning of the smelting process; therefore, a certain amount of ferrites, particularly magnetite, become slag. A significant part of  $\text{Fe}_3\text{O}_4$  is found from time to time in the slag as a suspension; therefore, slag with a high content of ferrites is viscous. Just like the ferrites, zinc sulfide influences the viscosity of the slag. One should specify that the solubility of  $\text{Fe}_3\text{O}_4$  and  $\text{ZnS}$  depend on the composition of the slag and the temperature.

The approximate composition of slag from reverberatory smelting (%) is shown below:

Cu	$\text{SiO}_2$	$\text{FeO}$	$\text{CaO}$	$\text{Al}_2\text{O}_3$	$\text{MgO}$	S	$\text{ZnO}$
0.15	54.0	15.7	16.2	11.8	-	-	-
0.12	43.4	27.9	9.2	12.3	2	0.1	-
0.40	29.4	44.8	2.7	10.2	0.4	-	3.7

#### MATTES FROM REVERBERATORY SMELTING

The matte is discharged from the furnace as it accumulates. In the interval between the discharges of the matte the tap holes are closed with corks made of refractory clay; debris is pushed through the cork and is hammered along by a hammer as its end dissolves in the matte. In order to discharge the matte the debris is pushed out, the matte flows along the gutter into a bucket, which is carried across by a bridge crane to the converter section of the shop.

Mattes from reverberatory smelting 80-90% by weight consist of copper and iron sulfides and contain 10-20% of oxides of other metals. It is not profitable to obtain rich mattes during reverberatory smelting since the physical and mechanical copper losses increase in slag. The majority of modern factories smelt mattes containing 20-35% Cu.

The approximate composition of mattes from reverberatory smelting is shown below (%):

Cu	Fe	S	Zn	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO + MgO
15.6	49.9	28.3	2.9	1.2	0.4	2.0
30.0	38.0	23.9	2.6	1.5	1.8	0.6
35.0	30.9	25.5	2.1	1.6	2.7	2.5
59.1	14.5	22.9	-	0.4	2.1	1.2

Au g/m	Ag g/m
8.7	230
7.8	168
3.8	600

Recovery of copper and precious metals in matte during reverberatory smelting reaches 95-99.5% because of the small yield of slag.

The daily smelting of the charge and the consumption of fuel are considered to be the technical and economical indices of reverberatory smelting: the latter is usually expressed in a conversion to comparison fuel (calorific value is 7000 kcal/kg) in percentage of the weight of the smelted charge. In modern plants smelting varies from 4.5 to 7 t. /tons/ of charge per 1 m<sup>2</sup> of the sole area. The most smelted is reached during the smelting of hot roasted concentrates, and the least-- during the smelting of unroasted highly siliceous concentrates, obtained as a result of enriching impregnated ore. Moreover, the smelting depends on the quality of the fuel, the design peculiarities of the furnaces and the quality of their servicing. The expenditure of comparison fuel comprises 11-25% of the weight of the charge.

#### Smelting Copper Concentrates in Suspension

The name of this process does not correspond to its nature. Reverberatory smelting in suspension is not possible since mutual contact of hard and liquid products is required for the necessary reactions to take place. The aggregate for smelting according to the method, about which we are talking, combines the usual reverberatory furnace and the furnace for roasting in suspension. The chief advantage of this set-up is the full maximum use of the heat, liberated during roasting, with a small expenditure of fuel. At the present time, this method of smelting, developed first in our country, is used in two foreign plants; in one of them air, enriched with oxygen, is used for roasting.

## SMELTING OF COPPER CONCENTRATES IN ELECTRIC FURNACES

Smelting of concentrates in electric furnaces is a version of reverberatory smelting. The method has a number of advantages, but as yet has limited use because of the high cost of electric power. The possibility of reaching high temperatures in electric furnaces considerably speeds up smelting, obtains highly siliceous slags which have a small specific gravity and sufficient fluidity (thanks to considerable excess heat). Due to the absence of flue gases, losses from dispersion of the charge decreases.

Heating and smelting of the charge takes place from the heat, liberated when the current passes through the layer of slag into which carbon electrodes have been lowered.

The consumption of electric power per ton of smelted charge is 400-500 kvt-ch [kilovolts per hour]; smelting indices which are close to those for reverberatory furnaces.

### # 38. TREATING COPPER MATTES

Further treatment of matte is identical regardless of the method by which it was obtained.

A modern copper smelting converter is made (to increase capacity and productivity) in the form of a horizontal cylinder along the generatrix of which tuyeres were placed to blow air.

The frame of the converter (Figure 95 and 96) consists of an iron shell lined inside with magnesite brick since quartz lining corrodes quickly.

Two smooth and one toothed rim are on the frame of the converter. Each smooth rim rests on two pairs of rollers fastened to oscillating bearings set in the foundation; the toothed rim is engaged with the transmission of the motor, and by means of this device the converter can turn to both sides.

In the middle of the frame there is an opening for loading the smelted matte and pouring off the smelting products which is called the top [throat], and in one of the face walls-- there is an opening for the pneumatic loading of fluxes during the smelting process.



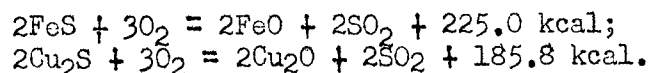
Gases, obtained in the operation of the converter, leave through the top, which in a operating position is turned upwards and is under an iron box--the dust screen, connected to the waste gaslines. The edge of the dust screen has a notch in the shape of the outside surface of the converter; therefore, it is closely joins the frame of the converter, preventing excess dilution of the gases with air, drawn from the atmosphere.

The converters operate periodically, smelting up to 100 t/tons of copper in one operation. The outside diameter of the converter is 3-4 m, and the length of the converter 6-9 m.

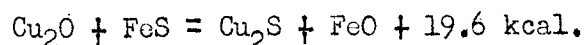
Matte scavenging is made up of two periods.

In the first period the iron is oxidized and slag is formed by adding quartz to it in the converter; the result is white matte and slag; the slag is poured off through the top.

Air, blown through the tuyeres into a layer of smelted matte, vigorously agitates the contents of the converter. Reactions from oxidation of sulfides take place on the surface of air bubbles;

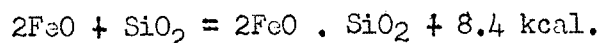


As a result of a double reaction with FeS, cuprous oxide is again converted to a sulfide:

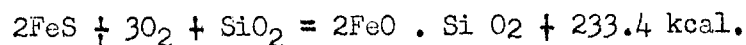


Thus, as a result of blowing the air in the first period only the oxidation of ferrous sulfide takes place. The formation of cuprous oxide is possible only after the oxidation of all the ferrous sulfide.

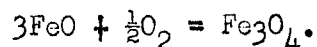
Ferrous oxide forms slag with the addition of quartz to the converter:



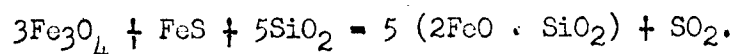
The oxidation of ferrous sulfide in the presence of quartz can also be expressed by the following total reaction which serves as the chief source of heat:



When quartz is lacking, ferrous oxide is oxidized to magnetite:

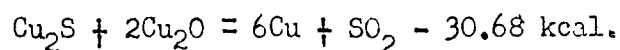


There is always a certain amount of ferrites in matte. The work of Professor A. N. Vol'skiy has shown the reducing power of ferrites with iron sulfide in the presence of quartz according to the reaction:



An equal supply of pulverized quartz to the converter to the surface of the matte and a sufficiently high temperature contribute to a complete reduction of the ferrites, the receipt of less viscous slag and a drop in the mechanical loss of copper in it. The ferrites, which have not been reduced during the blow, become slag, chiefly in the form of suspended hard particles, increasing the viscosity of the slag. After the iron is oxidized and the slag is poured off, the second period of the process begins.

Air continues to be blown over the white matte. The oxidation of  $\text{Cu}_2\text{S}$ , moreover, is accompanied by the formation of copper:



Crude copper contains a mixture of iron, sulfur, oxygen, zinc, nickel, arsenic, antimony, and other metals.

Gold and silver are practically completely transformed into crude copper because of their high solubility in mattes and copper and their poor solubility in converter slag.

Bridge cranes transport this smelted matte, which has been discharged from reverberatory furnace or the front hearth of the shaft furnace, to the converter in buckets. Before the matte is poured off, the converter is turned so that the tuyeres are above the layer of fusion.

The temperature of the matte which is poured into the converter is approximately 1100-1200°, and during the blow it swiftly increases because of the intensive oxidation of  $\text{FeS}$ . The normal temperature during the first period of work of the converter must be around 1250-1350°. Temperature must be observed within these limits in order to preserve the lining from premature wear and tear in order to obtain a sufficiently liquid slag. Increasing the temperature is done by adding smelted slag; lowering -- by loading coal aftercharges or by temporarily stopping the blast. Of course, each time that the blast is stopped, the converter must be turned so that the tuyeres come out from under the layer of the smelted mattes.

The quartz is loaded at the beginning of the blowing. When the quartz is supplied by a pneumatic gun, the quartz must be no coarser than 8 mm, but neither must it be very fine, and it must be easily

pulverized; when loading is through the top, the quartz can be coarser (up to 70 mm).

The smelted mattes must not occupy more than one third of the volume of the converter in order to avoid it being blown with air, and at the very same time, the surface of the layer of the matte must always be above the line of the tyeres. Therefore, after the slag has been blown and poured off, a new portion of raw matte is poured into the converter. The matte is loaded again, and the slag blown and poured off continuously until there is accumulated in the converter an amount necessary to convert to the second period of the process.

The length of the first period depends upon the contents of the copper in the matte and can vary from two hours until two days.

A small amount of iron always remains in the matte, and is finally oxidized at the beginning of the second period; therefore, in the second period a small amount of slag which is rich in copper is formed. After the copper has been poured off, this slag in the form of a pasty-like mass remains in the converter until the following operation. The second period usually lasts from two to three hours.

In its content converter slag is close to the silicate of ferrous oxide  $2\text{FeO} \cdot \text{SiO}_2$ ; the total content of the oxides of iron and silica is 75-90%; the remaining components fall into the slag by chance as impurities, contained in usable quartz flux. From their practice several factories have reached the following conclusions concerning the average data on the content of converter slag (%):

$\text{SiO}_2$	$\text{FeO}$	$\text{Al}_2\text{O}_3$	Cu
22-29	45-70	5-23	1.5-3.5

In order to extract any copper contained in them, converter slag soaks in a smelted condition in contact with the matte. In order to do this, the smelted converter slag is poured into an operating reverberatory furnace or into a front hearth or a shaft furnace; in some cases, the slag is poured off into an area and allowed to harden there, after which it is pounded into lumps and loaded into the charge of the shaft, smelting together with copper ores.

Because of the high degree to which air is used, converter gases of the first period contain 12-15%  $\text{SO}_2$  and the total of about 2% excess oxygen; the content of  $\text{SO}_2$  in gasses of the second period reaches 15-17%. Converter gases are quite suitable for obtaining sulfuric acid or sulphur; however they are seldom used for this purpose because of the periodicity of the work of the converters, and the strong dilution of the gases with air which is drawn from the atmosphere at the place where the dust screen joins the frame of the converter. Proposed

designs of hermetically sealed dust screens have still not yet been perfected, and they complicate servicing of the converters and have not been widely used. A majority of plants do not use converter gases and discharge them into the atmosphere through smoke stacks.

Dust, carried by converter gases, consists of hardened droplets of matte and copper, flux particles and volital oxides of impurities. The dust carries up to 1% copper (of the amount of treated copper) and precious metals. The chief amount of these valuable components is in a coarse fraction of dust, which is easy to catch in simple settling chambers. The dust from the chambers returns to the reverberatory smelting charge or to the converter. A thin fraction of dust can be settled only in electric filters, set up after the precipitating chamber. Oxides of lead and zinc are concentrated in a thin dust fraction.

Before the operation is completed the crude copper is poured from the converter into a bucket and carried to the casting site by a bridge crane. When there is only a little productivity, the copper is cast directly from the bucket into a fixed rectangular steel casting mold.

When the productivity is high, conveyor casting machines are used.

A conveyor casting machine is a conveyor belt to which are fastened casting molds which are filled from a collector similar to a mixer for iron, or from a bucket set up on special carriages. The speed of the conveyor belt is calculated so that copper, reaching the end of its horizontal part, hardens and cools somewhat. The copper ingot is discharged from the casting mold by tipping the latter.

The recovery of copper and precious metals from matte into rough copper, taking into consideration the treatment of converter slag, comprises 95 to 99%; the higher the percent is, the richer the matte is with copper.

The productivity of the converter depends upon the length of time it undergoes the blowing process, which varies in different plants from 75 to 90% of the operating time.

The cost of treating the matte depends to a great extent upon its composition. According to the calculations in one of the plants when the matte has a content of 13% copper, the cost of converting it is eight times greater than for matte which has 40-50% content of copper.

### # 39. SMELTING COPPER FROM TAILINGS

After sorting, the debris and tailings of the copper alloys are re-smelted in reverberatory or electric furnaces into various alloys. If it is necessary, the alloy, after it has been smelted, is refined and deficient metals are added in order that it may be brought up to a standard source. Then it is poured into casting molds and sent to the consumer.

Tailings which are difficult to sort (or strongly differ in content from standard norms) are refined into copper with the side extractions of other valuable components. Rough copper which is obtained from tailings is called secondary copper.

Tailings are sorted as to coarseness and a fine fraction forms clinkers in the clinker machines. Material that is 100 to 400 mm large is smelted.

The tailings are smelted into secondary rough copper in small shaft furnaces with a cross section near the tuyeres of 2-3.5 m<sup>2</sup>; the length of these furnaces is 2.15-3.45 m, the width 1-0.9 m and the height is about 6 m. Smelting is done using coke, the expenditure of which is approximately 12-17% of the weight of the charge; quartz and limestone are used as fluxes.

Copper oxides are easily reduced; therefore, only a weakly reducing atmosphere is necessary during smelting.

Zinc oxides are reduced in the lower portions of the SYP. Zinc and lead partially evaporate and are carried away by the gases. The main portion of these metals are converted into slag and the rough copper obtained during smelting. The yield of dust is 3-4% of the weight of the charge. The main mass of impurities is removed from the secondary rough copper during the blowing process in the converter. The temperature, necessary for the process, is created not only from exothermic reactions of oxidation of impurities, but also from burning coke which has been added to the converter. The consumption of coke is approximately 5 kg/t copper. Zinc, lead, and tin, which are oxidized during the blow, become slag and dust; the yield of the latter is 6-7% of the weight of the copper.

Converter slag is cooled, pounded into lumps, and fed to the shaft smelting charge. The content of zinc in converter slag reached 18-29%.

## # 40. REFINING COPPER

The average composition of copper smelted from primary and secondary material (%) is shown below:

	Cu	Fe	Ni	S
Primary copper	98.6-99.3	0.01-0.04	0.005-0.01	0.3-0.5
Secondary Copper	97.5-98.2	to 0.05	0.3-1.0	-

	Zn	As	Sb
Primary copper	0.03-0.6	0.01-0.1	0.01-0.1
Secondary copper	to 0.5	-	to 0.3

Moreover, rough copper almost always contains bismuth, tin, lead, selenium, tellurium, gold, silver, and dissolved gases, which even in small amounts lowers the mechanical properties of copper, especially its plasticity. All impurities, except for precious metals, lower the electrical conductivity of copper.

Rough copper frequently contains up to 100 g/t grams per ton of Au and up to 1000 g/t of Au. Precious metals are very valuable and must be removed from the copper when it is refined.

In the USSR commercial copper can be divided into five types corresponding to the field of use (Table 13).

Table 13

### CHEMICAL COMPOSITION OF THE VARIOUS TYPES OF COPPER

ACCORDING TO COST All-Union State Standard 859-41, %

Type of Copper, Copper	Content of impurities, no more than								
	No less than	Bi	Sb	As	Fe	Ni	Pb	Sn	S
M3	99.95	0.002	0.002	0.002	0.005	0.002	0.005	0.002	0.005
M1	99.90	0.002	0.002	0.002	0.005	0.002	0.005	0.002	0.005
M2	99.70	0.002	0.005	0.015	0.05	0.2	0.01	0.05	0.01
M3	99.50	0.003	0.05	0.05	0.05	0.2	0.05	0.05	0.01
M4	99.0	0.005	0.2	0.2	0.1	*	0.33	*	0.02

	O	Zn	Total Impurities	
MS	0.02	0.005	0.05	Note. The * shows the content of impurities permitted in the variety between the total content of all the impurities and the sum of the rest of the impurities.
M1	0.08	0.005	0.1	
M2	0.1	*	0.3	
M3	0.1	*	0.5	
M4	0.15	*	1.0	

There are two methods of refining copper -- the fire and the electrolytic method.

Pyro-refining [refining with fire] can produce types M3 and M4; bismuth and precious metals are not removed in pyro-refining.

Electrolytic refining produces copper which is very pure and recovers precious metals from it.

Electrolytic refining is more complex and more expensive than pyro-refining; however, the expense of refining copper with electrolysis is worth it, to a great extent, because of the precious metals obtained.

At the present time, because of the high demands for pure metals almost all of the smelted copper is refined by electrolysis. The quality of the refined copper is increased and the expense of refining becomes less if the main body of impurities is removed by the fire method. Therefore, electrolytic refining of copper is always preferable to the fire method.

It is easy to transport rough converter copper in the form of standard ingots (bars). It is frequently refined in special refineries, or pyro-refining can be carried out on the spot where it is smelted and the partially refined copper, which is in the form of specially shaped ingots (anodes), intended for loading into electrolytic baths, are sent to electrolytic refineries. The advantage of the latter method is that the pyro-refined tailings which are rich in copper can be re-processed in converters along with mattes.

#### PYRO-REFINING

The furnaces for pyro-refining (Figure 97) are similar to the reverberatory furnaces for smelting copper concentrates into matte. The capacity of the bath of the refining furnace is 400 t of copper, its depth is comparatively small--about 400-900 mm, the length is 15 m, the width 5 m, and the temperature necessary for the process is 1130-1150°.

The furnaces are heated with mazut, natural gas or pulverized fuel. A necessary requirement of fuel is that it lack or have only a small content of sulfur, since  $\text{SO}_2$  from furnace gases contaminates the refined copper with sulfur.

The bath or vat is laid out in a shell of cast iron slabs and set up on posts. Such a device prevents the copper from leaking through holes or loose parts in the construction. The vat is made of quartz or magnesite brick, the well of the acid ovens are faced with a mixture of fine quartz and copper cinder; magnesite with additions of lime, quartz, and iron cinder are used for building the well of the main ovens.

The wall of the furnace are lined with magnesite or highly-aluminous chamottebrick and the outside is faced with cast iron slabs and H-beams. Rectangular operating windows that are 1-1.7 m wide and approximately 0.8 m high are equipped with hoisting valves.

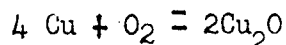
The arched crown is made of Dinas brick.

Ingot copper is loaded through the operating window with a shovel fastened to the trolley of the bridge crane (Figure 98); the shovel grasps up to 3.5 t of ingot copper; the smelter copper is poured by buckets by means of the crane or mixer-truck, which mixes up to 70 t of metal.

Pyro-refining of copper is a periodic process with a cycle of about 12-16 hours. Each cycle combines the following subsequent operations: smelting, oxidation of the impurities, removal of the dissolved gases, reduction of copper, and casting.

The impurities are oxidized with air, which is blown through iron pipes with a diameter of 10-20 mm submerged in the smelted copper. Oxidation takes place on the surface of the air bubbles, floating in the liquid metal. Copper and all the impurities, except for the precious metals, are oxidized.

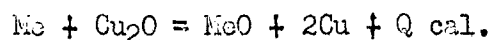
The speed of oxidation of each of the metals is proportionate to its concentration in the vat; therefore, copper is oxidized with the most speed according to the following reaction:



Ferrous oxide is dissolved in the smelted copper and because it is agitated with air blown over it, it swiftly spreads over the entire volume of the vat.



The impurities are oxidized according to the reactions, pictured in general by the equation:



The oxides of the impurities, floating on the surface of the vat, form slag, the removal of which from the surface of the vat, contributes to the process.

Lowering the concentration of free oxides in slag by combining them in weakly dissociated chemical compounds also contributes to oxidizing refining. This explains the excellent results of refining in furnaces with an acid sole where silicon dioxide, which becomes slag from the lining of the furnace, combines oxides in stable silicates.

The possibility of oxidizing the impurities not only with cuprous oxide, but also with oxides of other impurities, floating in the copper vat, explains the burning sequence of the impurities.

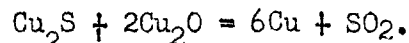
One can approximate that the sequence of oxidation of the impurities must correspond to the diminishing of these impurities' affinity for oxygen, that is according to the following order:

Al, Si, Mn, Zn, Sn, Fe, Ni, As, Sb, Pb, Bi.

Actually, all the impurities are burned simultaneously, but with different speeds which depend not only on their affinity for oxygen, but also on the ratio of concentrations, ability to form slag, speed of oxidation reactions, and a number of other reasons.

Precious metals, which have a lesser affinity for oxygen than copper, are not separated during pyro-refining, but bismuth is to a very small degree.

Sulfur is present in copper in the form of dissolved  $Cu_2S$ ; it oxidizes according to the following reaction:

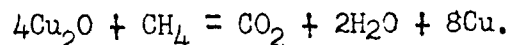


The affinity of selenium and tellurium for oxygen is less than that of sulfur; therefore, in oxidizing refining these elements are practically not removed.

The operation of removing gases dissolved in copper is called poling the density. Raw wood (rods and beams) are submerged in the vat of metal, cleaned of slag; vigorously escaping water vapors agitate the copper, contributing the removal of  $SO_2$  and other gases.

Then reduction is necessary in order to receive plastic copper since the content of soluble  $\text{Cu}_2\text{O}$  after oxidation can reach 10-12%.

Products of destructive distillation of wool--hydrocarbons, for example, are used as reducers:



In order to do this, the bath is covered with a layer of coal, and the wooden rods and beams are submerged into it for a longer period of time. Gas bubbles float onto the surface of the bath, the copper is well mixed, and the  $\text{Cu}_2\text{O}$  is easily reduced until only a residue remains (0.3 - 0.5%). The reduction of copper in factories is called malleability poling. The length of time of refining depends upon the size of the industry and its mechanization. When the smelted copper is either completely or partially loaded into the furnace, productivity increases considerably, since smelting occupies approximately 30% of the total length of the process; moreover, the expenditure of fuel decreases considerably.

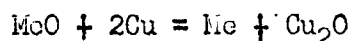
Reducing copper by blowing wood and coal dust or generator gas over the smelted bath shortens the length of time of this operation.

The end of the period of oxidation is determined according to the nature of a test for breakage; similar tests serve to determine the adequacy of the polings.

The slag is removed from the furnace (through operating windows) in the form of a pasty mass; sometimes it is "dry", loose, and more frequently viscous.

The prepared copper is discharged through a vertical slit in the wall of the furnace; to do this a dam of refractory clay gradually closes the covering slit. The copper is poured into the anodes, intended for electrolytic refining, in the turning-pouring machines (Figure 99). Cast iron or copper molds are filled with copper from a bucket with the capacity of approximately two tons which is attached to carriages; tilting, the bucket fills first one mold, after which the turning machine automatically turns, placing the second bucket under the lip. While it is turning in a circle, the copper hardens and is cooled with water from sprinklers. The prepared anodes are submerged into basins filled with water in order that they may be completely cooled, and then they are shipped to a warehouse.

Refining slags, before the copper is reduced, are carefully removed. If the slag is not removed then, when the content of  $\text{Cu}_2\text{O}$  in the bath is reduced, the impurities, which have accumulated in the slag, will be reduced from oxides and will again become copper;



The slag from acid ovens contains 15 to 40%  $\text{SiO}_2$ , 5 to 10% Fe in the form of silicates and ferrites, as well as oxides of zinc, nickel, and other impurities. The copper in this slag constitutes about 35 to 45%; approximately four-fifths of it is tied up in oxides, the rest of the copper is in the form of unsettled droplets of metal.

Slag from base ovens contain 50 to 75% Cu and usually no more than 5 to 10%  $\text{SiO}_2$ . The yield of slag constitutes 2 to 3% of the weight of copper. The slag is treated with reducing smelting in small shaft furnaces and is converted into rough copper and waste slag, and is further treated in converters when the mattes are blown.

### ELECTROLYTIC REFINING

Copper anodes are placed in a bath with a solution of copper sulfate and sulfuric acid. Thin sheets of pure copper, called cathode bases, are set up parallel to the anodes in the bath. Anodes are connected with a positive pole, and the cathode bases with a negative pole from the source of a direct electrical current. When the current passes, the anode dissolves, the copper is converted into a solution, and the ions of copper are discharged at the cathode bases, forming a layer of pure metal.

The anode, pictured in Figure 100, is 25 to 50 mm wide and weighs 150 to 350 kg. Thin sheets of electrolytic copper, obtained by die electrolysis of cold-rolled copper in bath especially intended for this, serve as cathode bases. After it has been carefully cleaned, the surface of the die is greased with fat, so that the residue of copper does not stick to the die. The electrolysis goes on uninterruptedly; after a day's work, the die is removed from the bath and the layer of copper which has accumulated on it is scraped off. Thus the sheets obtained are 0.5 - 0.6 mm thick.

The size of the cathode bases is 30 to 50 mm larger than the corresponding size of the anode. To the narrow edge of the sheet are fastened copper ears, to which a copper pole for suspending the bases in the bath and for conducting the current is passed.

The electrolytic bath (Figure 101) is a box made of wood or reinforced concrete, assembled on brick or concrete pillars 1.7 to 2.0 meters tall (for free passage under the bath, their inspection and repair), and are insulated with glass or porcelain packing. The internal surface of the reinforced concrete baths are lined with an acid-resistant slab and the wooden ones with sheets of vinyl plastic, welded together. Twenty to forty anodes are placed in the bath and more cathodes per unit. Alternating anodes and cathodes are placed parallel to each other.

The size of the bath depends upon the size and number of electrodes assembled in it. It is usually 3.5-5 meters long, 120 to 130 mm wider inside than the cathodes, and 1 to 1.2 meters deep. In order to feed it conveniently with currents, the 10 to 20 baths are connected in blocks; the bath of each block have a common long wall. The electrodes of the neighboring baths of the block are connected in series; to do this the ends of the cathode poles are placed on the little arms of the anodes of the neighboring bath. Indentations are sometimes made on the arms of the anodes for better contact. A diagram of the electrical current of the block of the baths is shown in Figure 102, and Figure 103 shows a general view of the electrolysis shop.

The voltage necessary to feed the apparatus is determined by the number of baths connected in series. In order to compensate the fall of voltage in the conducting wire, the calculated value of the voltage is increased by 10 to 15%. Even in small shops, the total required voltage rarely exceeds 500 volts; therefore, the electrolysis shop usually is fed from machine generators which have a larger efficiency coefficient than mercury arc rectifiers.

The electrolyte is mixed by a continuous circulation. From the supply tank the electrolyte leads into the long side of the block and is fed into each bath separately from one of its ends. A pocket, connected to the opening whose lower surface is below the bottom, is in the facing wall of each bath. The electrolyte, which has gone into the bath, flows from the opposite end through an outlet into a channel which is common to the entire block. The circulation speed is selected depending upon the electrolysis condition; usually the solution in the bath is renewed every one to five hours. The electrolyte flows along the over-flow channel into a collecting tank, and from the latter it is again transferred into the supply tank. Along the way from the supply tank into the bath, the electrolyte is heated with steam up to 50 to 55°. The expense of electric power comprises the major part of the cost of conversion. The expenditure of power is the specific index, calculated in kilowatt hours per ton of cathode copper; its value for the current and one bath are identical.

The amount of current, necessary to obtain one ton of cathode copper, can be computed according to Faraday's law. If 26.8 ampere-hours are needed to recover 1 gram-equivalent, that is  $\frac{57}{31.78} = 31.78$ g of copper from the solution, then the following will be expended for one ton:

$$IT_{\text{theor}} = \frac{1 \cdot 10^6}{31.78} \cdot 26.8 = 0.843 \cdot 10^6 \text{ ampere-hours,}$$

where I = current force, and T theor = time in hours.

Actually, not all the current is used to recover the copper; part of it is lost as a result of short-circuiting between the electrodes, the rise of side currents and a discharge of the ions from the impurities. The coefficient of useful current utilization (the yield according to the current) is equal to the ratio of the theoretically necessary amount of current to the actual expenditure of it;

$$K_T = I \cdot \frac{T_{\text{theor.}}}{I \cdot T_{\text{practical}}}$$

thus, the actual expenditure of current per ton of cathode copper comprises;

$$IT_{\text{practically}} = \frac{0.843 \cdot 10^6}{K_T} \text{ amp. hr/t}$$

In order to determine the expenditure of power, the amount of current must be multiplied by the fall of pressure between the electrodes;

$$W = (I \cdot T)_{\text{pract.}} \cdot V = 0.843 \cdot 10^3 \frac{V}{K_T} \frac{KVT - Ch/T}{\text{Kilowatt-hour/tons}}$$

The result obtained confirms the fact that the chief conditions for the economic behavior of electrolysis are a high yield of current and a small voltage drop in the bath.

The voltage in the bath is made up of the pressure, which is necessary to overcome the ohm resistance, and polarization. The difference of the potentials, necessary for dissolving copper at the anode and precipitating it at the cathode, is extremely small and it need not be calculated, since both electrodes are copper and the potentials in one and the same solution are practically identical. Therefore, the voltage in the bath is chiefly expended to overcome the ohm resistance of the electrolyte.

The resistance of the electrolyte is lowered by increasing the concentration of copper sulfate and sulfuric acid; the limit of this is the common solubility of these substances in water. The resistance of the electrolyte decreases when the temperature increases.

The compositions of the electrolyte, chosen through long years of factory practice, lies from 30 to 40 g/l [grams/liters] Cu and approximately 200 g/l of  $H_2SO_4$ .

Polarization is another component of voltage drop in the baths which is essential in value. The copper ions transfer the current from the anodes to the cathodes by diffusion. The speed of diffusion is not great and only in certain limits can it be increased by agitating the electrolyte. When the current has a great force, the speed of transference of the ions of copper into the solution of the anode and their discharge at the cathode can be faster than the speed of diffusion. In addition to this, in the layer around the anode, the concentration of copper will be greater, and in the layer around the cathode it will be lower than in the remaining mass of the solution. The potential of the anode is increased, and the potential of the cathode is decreased when compared with the equilibrium potential for the initial solution, and a difference of potentials will arise between the electrodes directed oppositely from without, causing an additional drop in the voltage. When the force of a current is constant, the value of polarization depends upon the area of the electrodes; therefore, polarization must coincide with the force of the current, entering per unit of the area of the electrode, usually the cathode (that is, from the cathode density of the current); the higher it is, the greater will be the fall in the voltage in the bath because of polarization. Agitating and heating the electrolyte lowers polarization. By increasing the density of the current, the fall of the voltage in the ohm resistance of the electrolyte will essentially increase. An example of the balance in the bath is shown in Table 14.

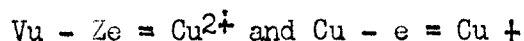
Table 14

BALANCE OF VOLTAGE IN BATH DURING  
ELECTROLYSIS OF COPPER

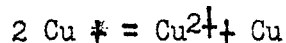
(according to A. Gaev and O. Esin)

Section of Bath current	Fall of Voltage	
	Volts	%
Electrolyte.....	0.23850	80.5
Polarization.....	0.01587	5.3
Slimes.....	0.02025	6.7
Cathodes and Anodes.....	0.00337	1.1
Contacts.....	0.01829	6.4
Total.....	0.29638	100.0

When the anode dissolves the copper goes into a solution in the form of bivalent and partially monovalent ions according to the diagram;

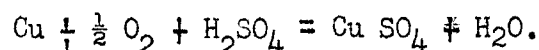


However, the ions of the monovalent copper in the electrolyte are unstable and they immediately form bivalent ions;



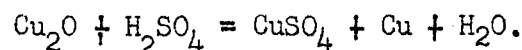
in addition to this, the precipitate of elementary copper falls to the bottom of the bath.

To a certain degree dissolving the anode is possible by chemical means when the oxygen from the air participates:



The impurities are less precious than the copper of the metals; zinc, nickel, lead, arsenic, tin, antimony, and bismuth are dissolved in the electrolyte just like copper.

The impurities of the precious metals -- gold and silver -- as well as the impurities which are in the anodes in the form of chemical compounds with sulphur, selenium, and tellurium, settle at the bottom of the bath in the form of hard particles, forming slime. Cuprous oxide is dissolved in the sulfuric acid and the copper settles out:



The lead ions which have been formed when the anode dissolved are joined in an insoluble sulfate.

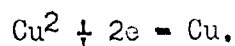
The ions of arsenic, antimony, tin, and bismuth, are treated with hydrolysis, forming arsenous, antimonous, and stannous acid, as well as the basic sulfuric salt of tin and bismuth. All these compounds are hard to dissolve in the electrolyte and a great part of them become slime.

The slimes precipitate at the bottom of the bath, but part of them remain on the surface of the anodes in the form of a crust which increases the ohm resistance of the circuit of the bath (see Table 14). The very finest light particles of slime remain for a long time in a suspended condition in the electrolyte and form the so called floating or wandering slime. The composition of the slime depends upon the composition of the anodes and other reasons: their approximate composition is shown in Table 15.

Table 15

APPROXIMATE COMPOSITION OF SLIME, %									
Slime	Cu	Pb	Bi	Sb	As	Ag	Au	Se	Te
From Bath Bottom	14.3	2.4	0.5	5.5	2.7	35.0	0.6	5.7	2.7
Wandering	0.6	2.8	0.5	48.5	17.8	0.04	-	-	-

Copper precipitates at the cathode as the result of the discharge of ions according to the following diagram:



Metals which have gone from the anodes into the solution along with copper -- zinc, nickle, iron, and others -- have considerably less potentials of discharge than copper. They can not, therefore, precipitate at the cathode along with copper, and they accumulate in the solution. Even when the impurities have accumulated to a great degree in the electrolyte, their ions do not discharge at the cathode.

The copper crystals which have grown on the cathode and which have taken hold of the electrolyte and the particles of wandering slime chiefly expalins the contamination of the cathode precipitate by impurities which have been observed in practice. Therefore, the degree of precipitation contamination grows as the impurities accumulate in the electrolyte. In order to prevent this, part of the electrolyte is periodically taken out of circulation and replaced with a fresh solution of sulfuric acid. Practice has shown the following approximation norms for the content of impurities allowed in the electrolyte (g/l):

<u>As</u>	<u>Sb</u>	<u>Fe</u>
15	6	3

Contamination of the precipitate by wandering slime is dangerous when there is a high current density, suitable from the point of view for increasing productivity of electrolysis. When the current has a high density, polarization grows, and consequently, the voltage in the bath and the expenditure of energy increases; therefore, in order to lower polarization, circulation of the electrolyte must be increased, resulting in the slime becoming turbid and the cathodes becoming contaminated with it.

Copper is separated out at the cathode in the form of a stable precipitation; however, uniformity of its growth is destroyed with



the passage of time, and on the surface of the precipitate there will appear unevenness, protuberances, bumpy knots; the protruding parts grow faster since in the places where they arise the resistance between the anode and the cathode decreases. The uneven and loose precipitate encompasses a great part of the electrolyte and the wandering slime; moreover, the unevenness of precipitation of copper frequently causes short-circuiting between the anode and the cathode. Small additions of certain surface-active substances in the electrolyte -- joiner's glue, gelatin, tannin, machine oil, tailings from the cellulose industry -- contributes to the receipt of even and denser cathodes, as well as to an improvement in their purity. The expenditure of these substances goes from tenths of parts of a gram to tens of grams per ton of copper.

All the anodes are simultaneously submerged into the bath by a bridge crane to which has been suspended a frame with a claw, which is called a harrow, and the cathode bases are also submerged.

Dissolving the anode usually takes from 20 to 30 days and depends upon its thickness.

Anode precipitates, constituting 8 to 15% of the primary weight, is re-smelted into new anodes.

The cathodes are taken out every 7 to 15 days. At the time that they are removed, the weight of each of them is 60 to 40 kg; allonger accumulation of the cathodes is unsuitable because of the frequent short circuiting, caused by an uneven growth of the precipitate. After they have been carefully washed, the cathodes are again smelted. During the loading and unloading alternate baths short circuit, not destroying in this way the work of the series circuit.

The usual force of the current in a circuit of the bath is 10,000 to 15,000 amperes; the voltage in the bath is about 0.3 volts. The density of the current is selected depending upon the purity of the anodes (Table 16).

Table 16

APPROXIMATE DENSITY OF CURRENT DURING ELECTROLYSIS OF COPPER

Content of copper in anodes, %	Permissable cathode current density a/m <sup>2</sup>
96 97	85 - 90
98 99	100 - 120
99.5 - 99.8	200 - 400

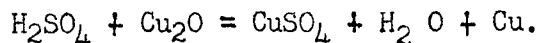
Servicing the bath results in a timely elimination of short-circuits and the supervision of the purity of the context, temperature of the electrolyte, and voltage.

The yield in current in modern factories reaches 98%. The expenditure per ton of cathode copper is 200 to 300 kilowatt hours.

### REGENERATION OF THE ELECTROLYTE

Restoring the electrolyte (regeneration) is necessary in order to prevent the accumulation of impurities and the removal of the excess copper.

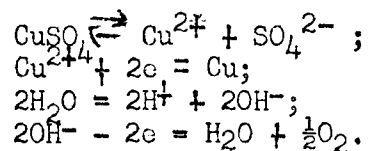
The copper is accumulated in the electrolyte because it is only partially dissolved by chemical means with the participation of the oxygen from the air;



In addition to this, there is 1.5 to 2% more copper in the electrolyte than that which precipitates at the cathode.

The copper sulfate which has been gradually accumulating in the solution can begin to crystallize especially on the surface of the anodes since in the layer around the anode its concentration is always very high. The electric conductivity of the electrolyte becomes worse as the copper accumulates.

If the content of the impurities is not great and the excess of copper only needs to be removed, the electrolyte is treated with electrolysis in baths which are of the usual construction, but equipped with insoluble anodes. The copper from the electrolyte, moreover, precipitates at the cathodes, and the oxygen separates at the lead anodes:



Free sulfuric acid is formed in the solution. After part of the copper has been removed, the solution can be returned to the circulation system. The voltage at the bath during electrolysis with the non-soluble anode, which is composed of potentials for removing the copper and oxygen, comprises about 2 to 2.5 volts; the expenditure of power in these baths is approximately ten times more than during the electrolysis with soluble anodes.

If it is necessary not only to lower the content of copper, but to remove the impurities, for example, so that the sulfuric acid may be used again, then the electrolytic method is not feasible, since only after all the copper has been separated by the electrolysis can we succeed in removing the impurities; the copper from poor solutions precipitates in the form of loose precipitate which has been contaminated with impurities, and it is expensive to clean the solution any further.

In this case part of the electrolyte which has been removed from circulation is neutralized with copper dross or with copper that has been heated by blowing air over it (in order to speed up the dissolving of copper). The hot solution is poured into special baths, where the crystals  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  precipitates from it. The mother solution evaporates and again crystalizes, forming an additional amount of copper sulfate [copper vitriol]. Vacuum apparatus is used in modern enterprises for evaporation and crystalization. The combined method of regeneration is most frequently used. This is where one portion of the electrolyte only is depleted of copper by electrolysis and returned to circulation; the other portion of the electrolyte is converted into copper sulfate, and the main mass of copper is removed from the final mother liquid by electrolysis, and nickel sulfate is crystalized since nickel always accumulates on the electrolyte.

After it has been carefully washed, the cathodes are smelted in reverberatory or electric ovens. The copper is cast in ingots of a standard form weighing 80 to 85 kilograms.

Recently a great deal of attention has been paid to the production of oxygen-free copper, which has improved softness, plasticity, and electric conductivity. In order to have oxygen-free copper, the cathode copper is smelted and is cast in an atmosphere of regenerator gas.

The slime is retreated in order to recover copper, precious metals, selenium, and tellurium.

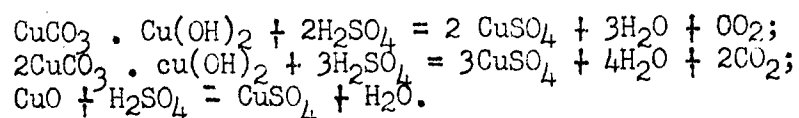
#### # 41. Hydrometallurgy of Copper

Only the mineral chalcantite [blue vitriol]  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  of the natural compounds of copper is quite soluble in water. The other copper minerals are really not soluble at all in water, which is leaching. The method, based on the transformation of copper minerals into sulfate, is called the sulfuric acid method; sulfuric acid and sulfate of ferric oxide are used as reagents.

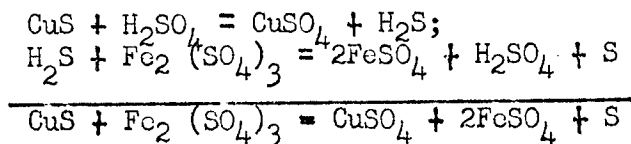
The method by which complex ammonia salts of copper are formed is called the ammonia method; ammonia and ammonium carbonate here serve as reagents.

### SULFURIC ACID METHOD

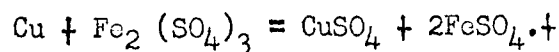
The sulfuric acid method for treating copper ore is based on the fact that sulfuric acid reacts in a water solution with carbonates and oxides of a bivalent copper;



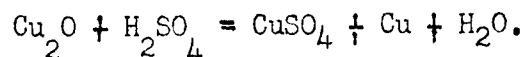
Copper sulfides slowly react with weak solutions of sulfuric acid because of the formation of comparatively strong dissociated hydrogen sulfide; the reactions are speeded up in the presence of an oxidizer; the sulfate of ferric oxide is used for this:



Natural copper does not displace hydrogen from sulfuric acid but easily forms sulfate in the presence of an oxidizer;



Cuprous oxide is not converted into sulfate in the action of only sulfuric acid; one atom of copper slips off, moreover, into the elementary form:



Cuprous oxide with a mixture of sulfuric acid and an oxidizer are completely converted into sulfate.

Cuprous sulfide, as well as the higher sulfides of copper -- chalcopyrite and bornite -- are converted into sulfates by the action of sulfuric acid and iron oxide sulfate.

In order to avoid large expenses for heating considerable masses of ore and solutions, the leaching is carried out in the cold.

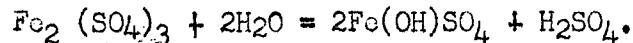
Solutions containing  $\text{CuSO}_4$ ,  $\text{FeSO}_4$ , an excess of reagents ( $\text{H}_2\text{SO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$ ) and impurities, are separated from the non-soluble residue by settling or filtering.

In order to separate the copper from solutions, electrolysis can be used (lead sheets serve as anodes, and thin sheets of pure copper serve as cathodes). During the electrolysis the ferric iron is reduced at the cathode until it is ferrous iron:

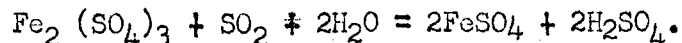


Due to the fact that when there are large amounts of excess ferric oxide sulfate present, the yield of copper in the current is lowered considerably.

In order to avoid excessive expenditure of current to reduce iron, the solution before electrolysis is either completely cleaned of the iron or the iron is reduced until it is ferrous iron to the action of sulfur dioxide. In order to clean it from iron the solution is neutralized with excess sulfuric acid -- by agitating it with a thinly pulverized copper ore, as a result of which the ferric oxide sulfate is treated with electrolysis when the acidity is lowered thus forming basic iron sulfate of various types which are very little soluble, for example:



The reduction of ferric oxide by sulfur dioxide takes place according to the following reaction:



Complete separation of copper from the solution by electrolysis is economically not feasible, since the electrolysis of poor solutions takes place when there is very little energy used because of the joint discharge of hydrogen ions. Complete separation of copper from solutions which have not been cleaned of iron is even more unfeasible. The solution, which has been taken from the electrolytic baths after the necessary amount of copper has been separated, is called the spent electrolyte. It contains the sulfuric acid which was formed during the electrolysis and can be used again for leaching copper from ore (Table 17).

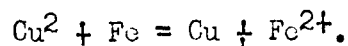
Table 17

APPROXIMATE COMPOSITION OF SOLUTIONS DURING HYDROMETALLURGICAL  
EXTRACTION OF COPPER FROM ORE

Solution	Cu	H <sub>2</sub> SO <sub>4</sub>	Fe <sub>total</sub>	Fe <sup>3+</sup> †	Fe <sup>2+</sup> †
Strong after leaching	42	25	2.5	0.7	1.8
Reverse spent electrolyte	30	58	2.5	2.0	0.5

If the ore does not contain sulfide and native copper then the presence of ferric oxide sulfate in the solution is not needed and the complete cleansing of the solution from iron before electrolysis takes place is feasible. If the ferric oxide sulfate is necessary for leaching, then it is confined only to reducing it before electrolysis to oxide sulfate.

The copper, which has been left in the electrolyte after electrolysis, circulates with the solution, which gradually becomes contaminated with impurities; therefore, periodically part of it is removed and replaced with sulfuric acid. From the part of the solution which has been removed, the copper is separated by cementation by scrap iron according to the following reaction:



An example of a simplified technological diagram of the sulfuric acid method for recovering copper from ore is shown in Figure 104.

The speed of leaching copper depends upon the speed of diffusion of the reagent inside the grains of ore. The finer that the ore is pulverized, the less time is needed to convert copper from ore into a solution. Ore which has a dense structure and fine impregnation of minerals requires finer pulverization than loose and porous ore. Pulverization is an expensive operation; therefore, it is necessary to choose the size by experimentation which is applicable to the peculiarities of the treated ore.

Agitating the solution speeds up leaching, contributing to an exchange of substances in the pores of the lumps of ore. The agitation method is selected depending upon the size or coarseness of the ore which will be leached. The grainy (sandy) material is leached, percolating through the solution through a fixed layer of ore. This

method is not suitable for fine (filtered) ore; the fine particles lie in a dense layer, and it is difficult for the solutions to penetrate. Therefore, ore which must be finely pulverized is leached into pulp; the particles of ore are held in a suspended condition by continual agitation. The percolation method of leaching is more expensive than pulp leaching because of fewer expenses for crushing the ore and agitating; therefore, such leaching has the advantage in the hydrometallurgy of copper, especially when treating poor ore.

The vats for leaching by percolation are usually made of reinforced concrete; the inside surface is lined with an acid-resistant brick, acid-resistant mastic, or faced with sheet lead. In the latter case, the inside surface of the vat is faced with wood for the protection of the lead. The vat is a rectangular box 30 to 50 meters long, 20 to 35 meters wide, and 5 to 6 meters tall. At the bottom of it is a screen made of wooden cross bars, on top of which is a false perforated bottom made of boards and covered with matting or filtering cloth. The ore that is about 10 mm large is loaded by means of a crane; the vat holds 8,000 to 10,000 tons of ore. If many fine particles which hamper the percolation of the solution are obtained during the crushing operation, the fines are first removed by sifting or by wet classification. The solution is either fed on the side through an opening under the false bottom and percolated through the layer of the ore from above and is then poured into the upper part of the vat, or it is poured from above and is removed through the opening under the false bottom.

Leaching usually takes from 7 to 15 days and can either be periodic or continual. When the leaching is handled periodically, the vat is filled with the solution and it remains in that condition for a definite length of time, after which the solution is poured off and the vat is filled with a new portion of solvent.

When the leaching is continuous in a system of several vats joined together in series, the solution continually flows from vat to vat using the counter-flow principle: a fresh solvent is fed into the leached ore and is removed from the system after it has come in contact with the freshly loaded ore.

One vat is always being loaded and the other unloaded.

The spent ore is removed from the vat by grab cranes or hydraulically, washing it with a strong stream of water and removing the pulp obtained channels.

The vats for leaching silt are either pneumatically or mechanically agitated. Their design is described in the chapters concerning the metallurgy of zinc and the metallurgy of gold.

Pulp leaching is used for fine fractions of ore, which are not suitable for loading into the vats for percolation leaching, or when the ore is treated with a fine impregnation of minerals, requiring fine pulverization.

The pulp from the leached ore is sent into thickeners. The clarified solution is further treated for the removal of copper from it (through electrolysis or cementation). The thickened product is filtered in vacuum filters, washed with ore and taken away as waste.

The filtrate and the washing water join the spent solution of thickeners and are used to prepare the initial pulp.

The extraction of copper by the sulfuric acid method from ores which contain 1 to 1.5 Cu reaches 88 to 94%.

#### THE COMBINED SULFURIC ACID METHOD FOR THE RECOVERY OF COPPER FROM ORE

The methods for leaching with sulfuric acid which has been described above are suitable primarily for oxidized ore. Even through the joint action of sulfuric acid and iron oxide sulfate the copper is not completely extracted from some of the sulfide minerals. During the sulfuric acid method precious metals are lost in the tailings.

The combined process, suggested by Professor Z. Ya. Mostovich and Professor Z. A. Zanyukov, makes it possible to extract copper and precious metals from mixed copper ore. The merit of this method lies in the fact that it excludes the expensive and labor-consuming filtration of the tailings.

The essence of the method lies in the leaching of the oxidized copper with sulfuric acid and subsequent cementation of the dissolved copper directly from the pulp by active sponge iron. The cemented copper which has precipitated is further floated along with sulfide minerals and gold, if there are any in the ore. The gold is also extracted because it is associated with the sulfide minerals. The concentrate obtained is treated with the pyrometallurgical method.

#### THE AMMONIA METHOD

The ammonia method is based on the ability of certain minerals of copper to react with water solutions of ammonia and ammonium carbonate,

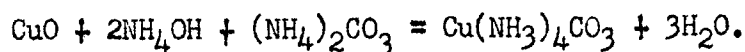


forming complex ammonia-copper salts which are very soluble in water.

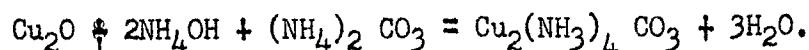
The base copper carbonate, which is in nature as the mineral malachite and azurite, react with ammonia and ammonium according to the following equation:



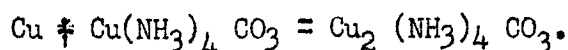
The mineral melaconite reacts in an analogous way:



Cuprite forms a complex salt of monovalent copper:

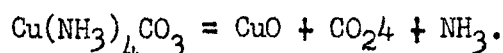


Native copper is oxidized by an ammonium complex of oxide and is converted into solution as a result of the following reaction:



Copper sulfides do not react with ammonia and ammonium carbonate; therefore, the ammonia method can not be used for ores which contain sulfide copper.

Complex ammonia-copper salts are decomposed when the solutions are heated with live steam; moreover, the cupric oxide and to some extent cuprous oxide usually precipitate out;

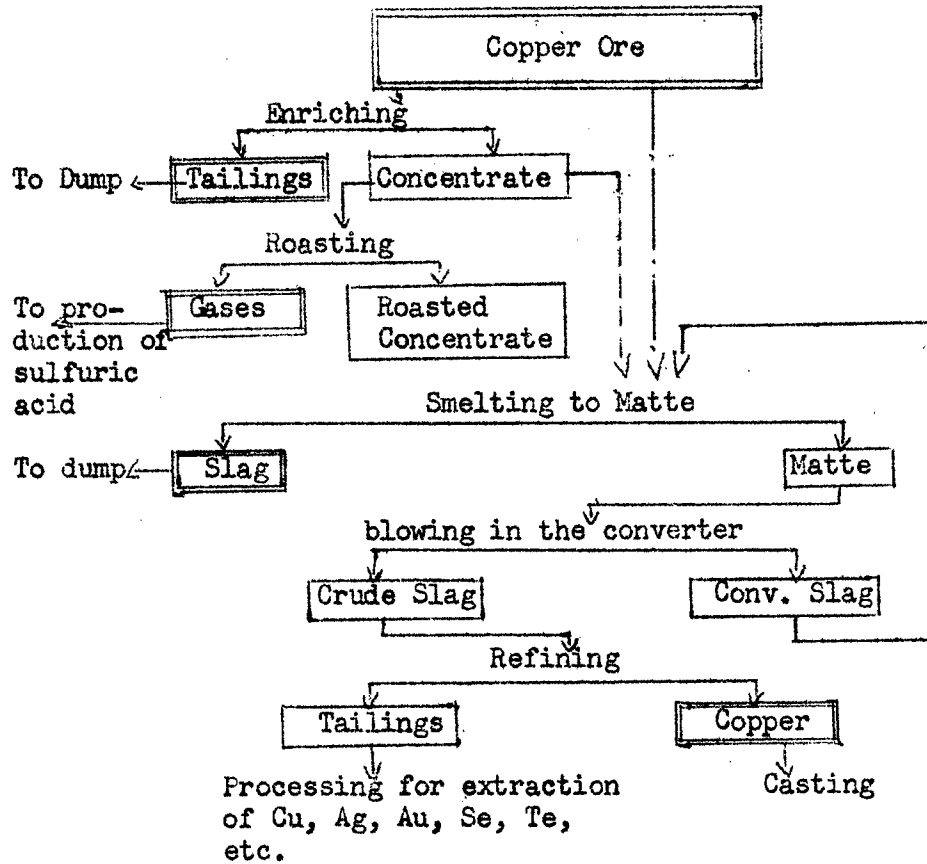


The ammonia and carbonic acid which are separated from the solution are absorbed by the water and are again used to treat the ore.

Leaching copper with ammonia and ammonium carbonate is accomplished by the percolation method in round iron vats, hermetically sealed. The vat houses about 500 tons of ore. The most concentrated solutions obtained during the leaching contain up to 80 g/l Cu. Part of the strong solution is used to settle copper, effected by blowing live steam at a temperature of 100 to 130° through the solution. Moreover, the gas-like ammonia which has separated out is caught in towers sprinkled with water. The cupric oxide precipitate undergoes reducing smelting; the filtrate joined with the solution of ammonia from the absorbing towers again undergoes the leaching process.

The defects of the ammonia method, besides its inapplicability to sulfide ores, is the necessity of hermetically sealed apparatus and the high cost of reagents.

FIGURE APPENDIX



\_\_\_\_\_.\_\_\_\_\_ Direct smelting of ore  
 - - - - - Smelting the concentrate without burning

Figure 87. General diagram for obtaining copper by pyrometallurgical method

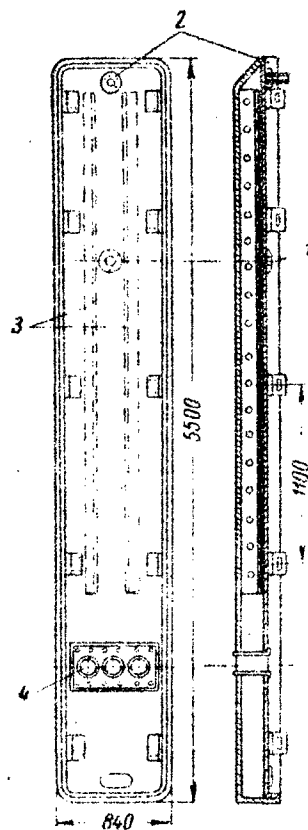


Figure 88. Caisson of shaft furnace:

- |                 |                         |
|-----------------|-------------------------|
| 1. water feed   | 3. rigid ribs           |
| 2. water runoff | 4. openings for tuyeres |

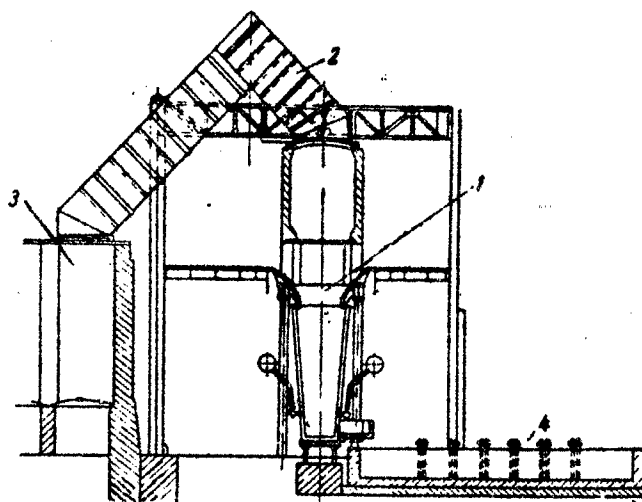


Figure 89. Arrangements of shaft furnace and front hearth in the shop:

- |             |                 |
|-------------|-----------------|
| 1. oven     | 3. dust chamber |
| 2. gas line | 4. front hearth |

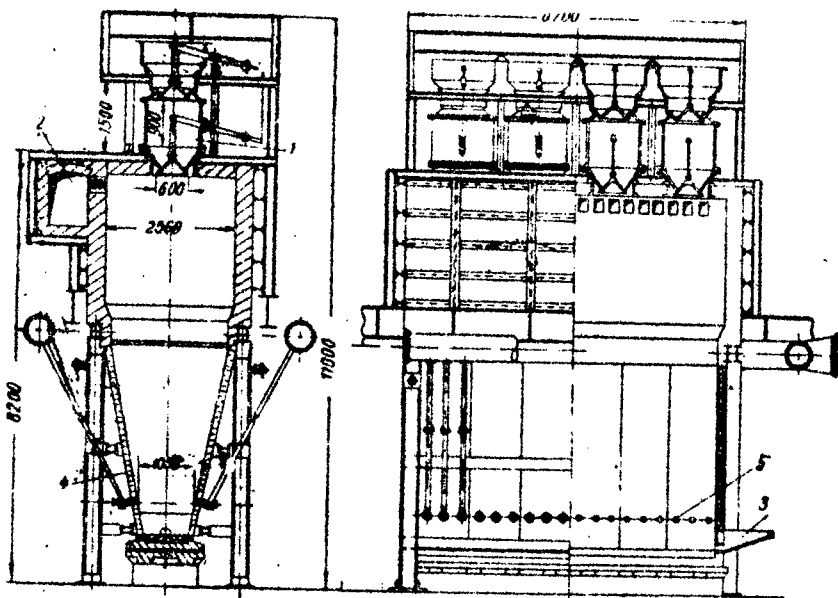
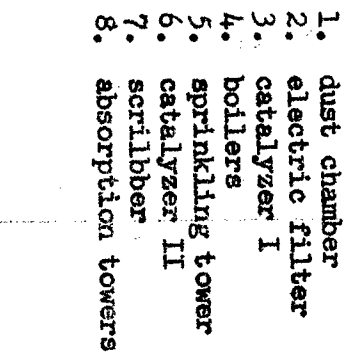


Figure 90. Shaft furnace for copper-sulfur smelting:

1. loading device
2. gas outlet
3. drain chute
4. caissons
5. tuyeres



Legend:

1. Slag
2. Matte
3. Concentration
4. Reverse matte
5. Coke, flux
6. Ore
7. Ore Smelting
8. Slag
9. Gases
10. Dust
11. Thin dust

12. Water
13. Steam
14. Sulfur
15. Sulfur
16. Sulfur
17. Tailings
18. Warming gas
19. Precipitated sulfur (milk of sulfur)
20. Water
21. Solution
22. Cases

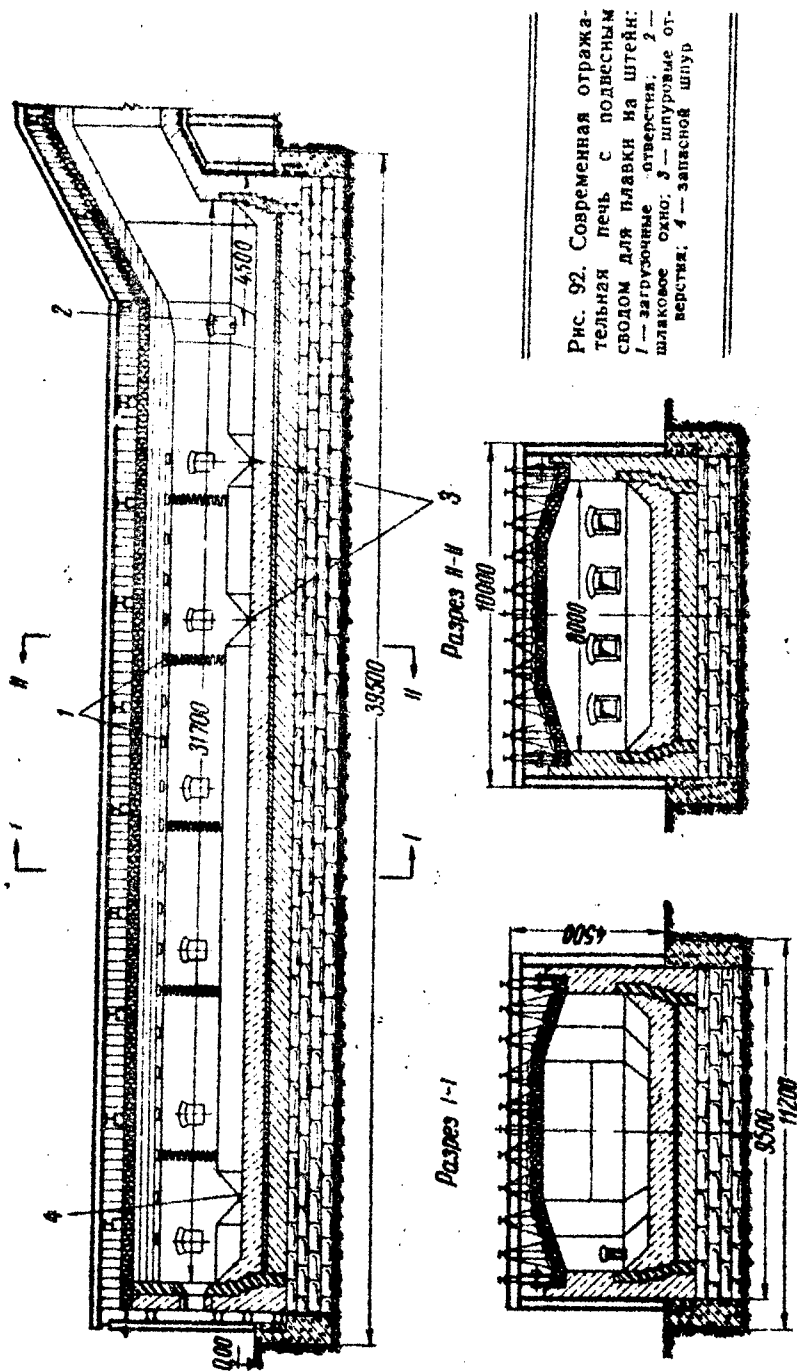


Figure 92. Modern reverberatory furnace with suspended crown for smelting to matte:

1. Loading openings
2. slag window
3. blast holes
4. auxiliary blast hole

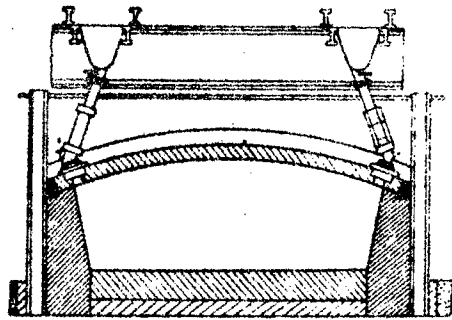


Figure 93. Arched crown of reverberatory furnace.

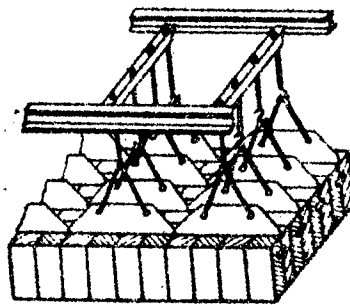


Figure 94. Diagram of suspended magnesite crown.



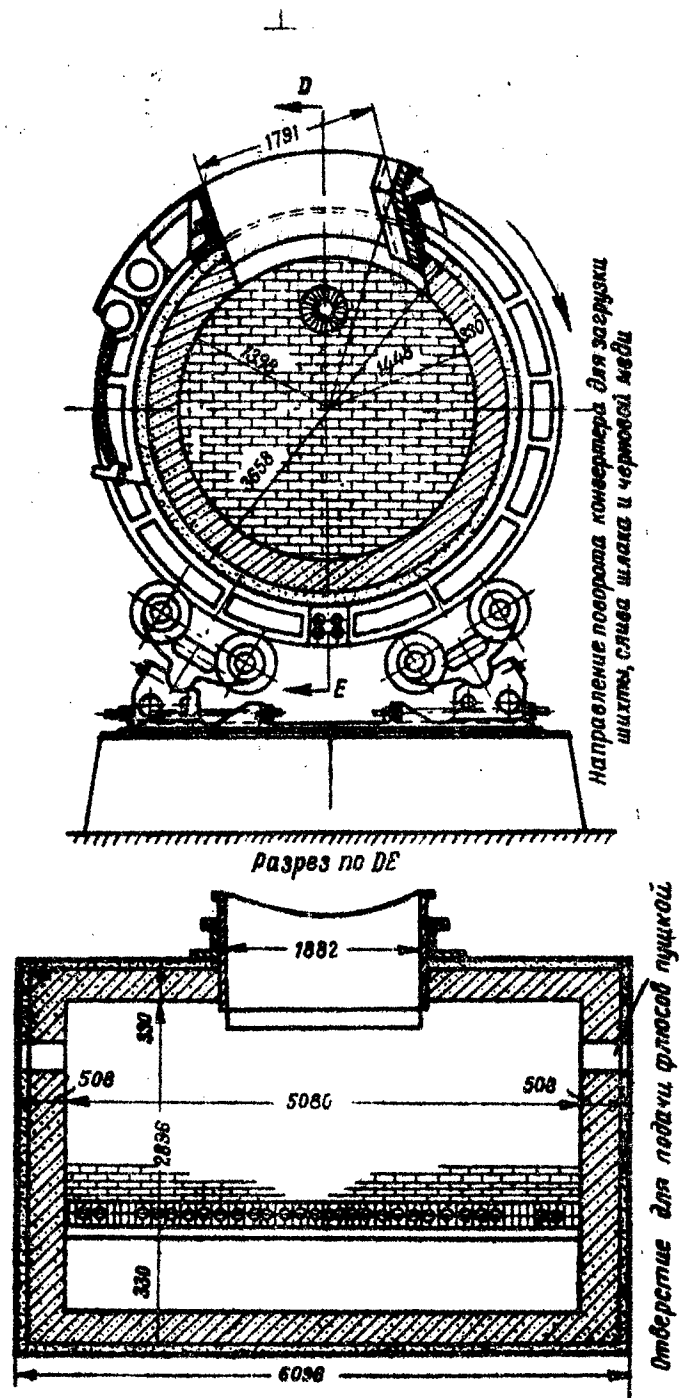


Figure 95. Top - Direction of turn of converter for loading charge, discharge of slag and rough copper. Below - Opening for supplying flux by gun. General title - Converter for blowing matte.

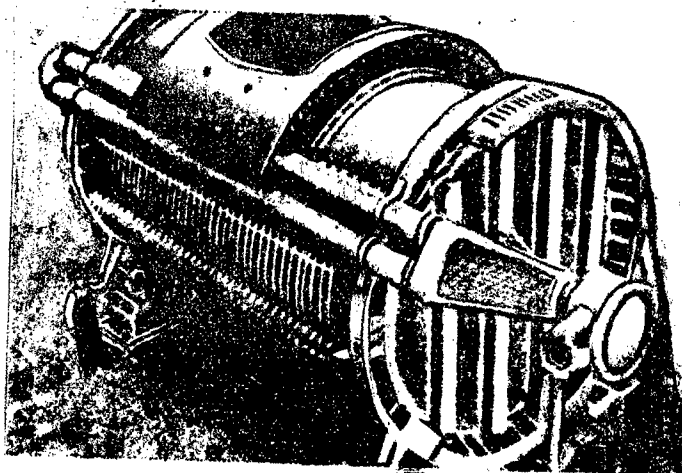


Figure 96. General view of converter.

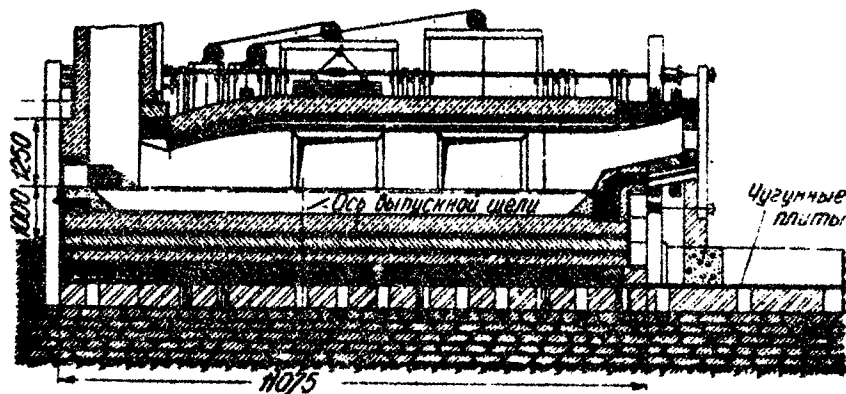


Figure 97. Furnace for pyro-refining of copper.

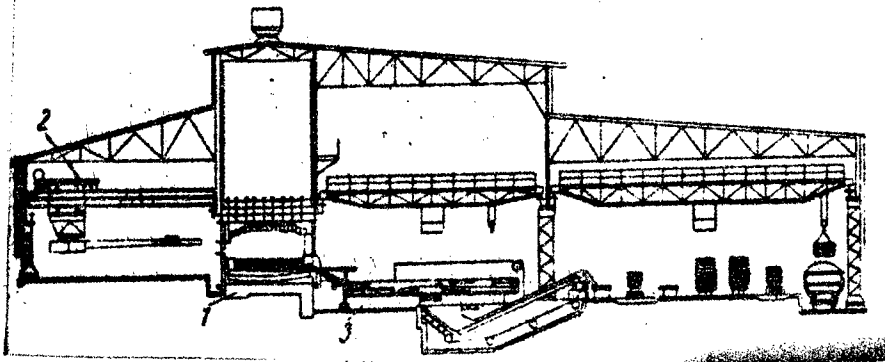


Figure 98. Shop for pyro-refining of copper.

1. refining oven
2. crane for loading copper
3. casting machine

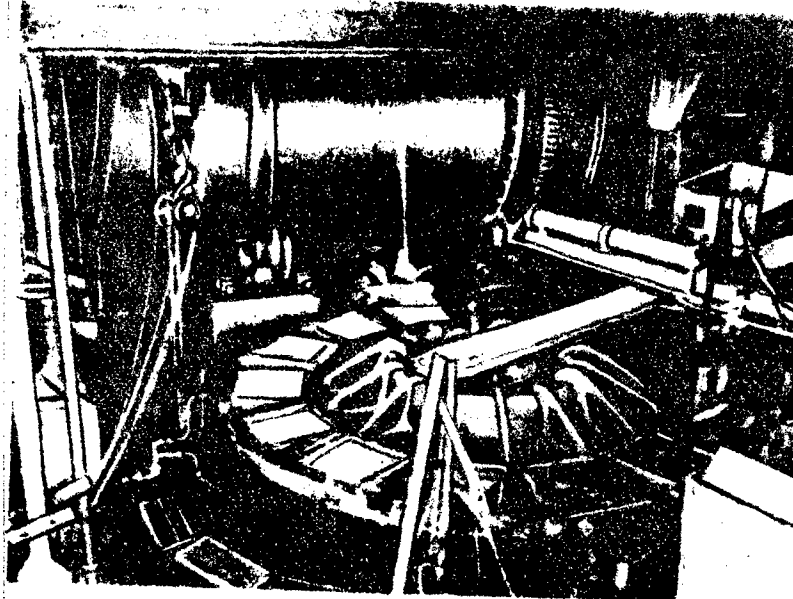


Figure 99. Casting anodes in rotating casting machine.

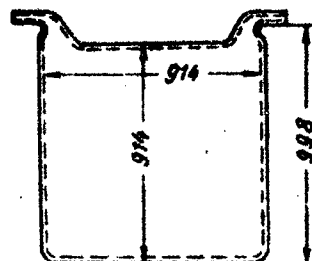


Figure 100. Anode

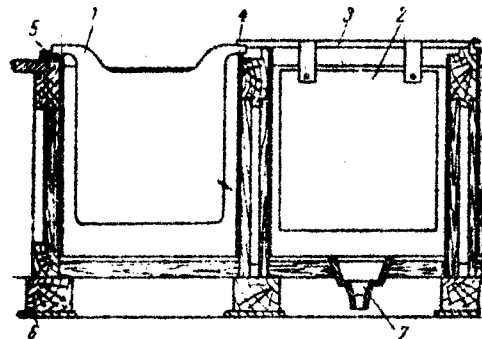


Figure 101. Bath for electrolysis of copper.

- |                     |                                  |
|---------------------|----------------------------------|
| 1. anode            | 5. anode bus bar                 |
| 2. cathode          | 6. insulation                    |
| 3. cathode rod      | 7. outlet for discharge of slime |
| 4. place of contact |                                  |

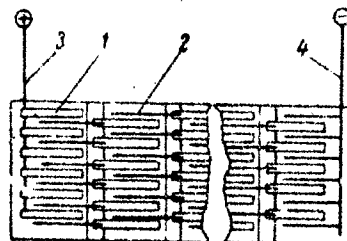


Figure 102. Diagram of electrical circuit of baths:

- |             |                    |
|-------------|--------------------|
| 1. anodes   | 3. anode bus bar   |
| 2. cathodes | 4. cathode bus bar |

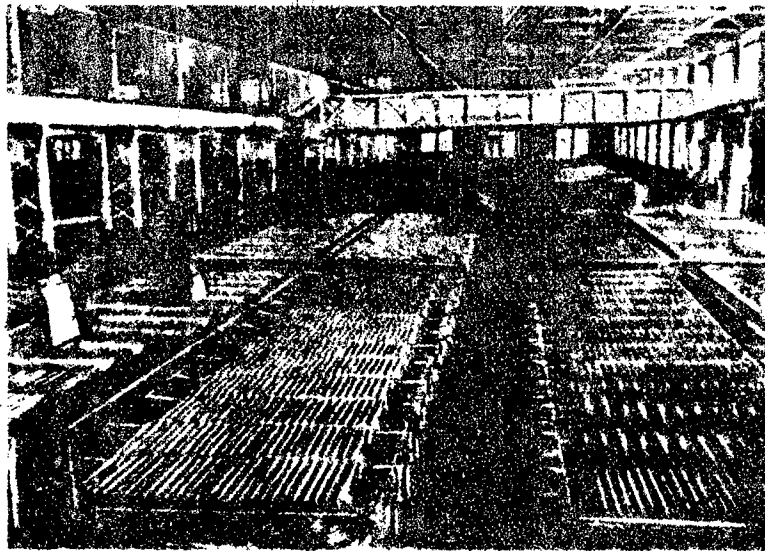


Figure 103. General view of electrolysis shop.

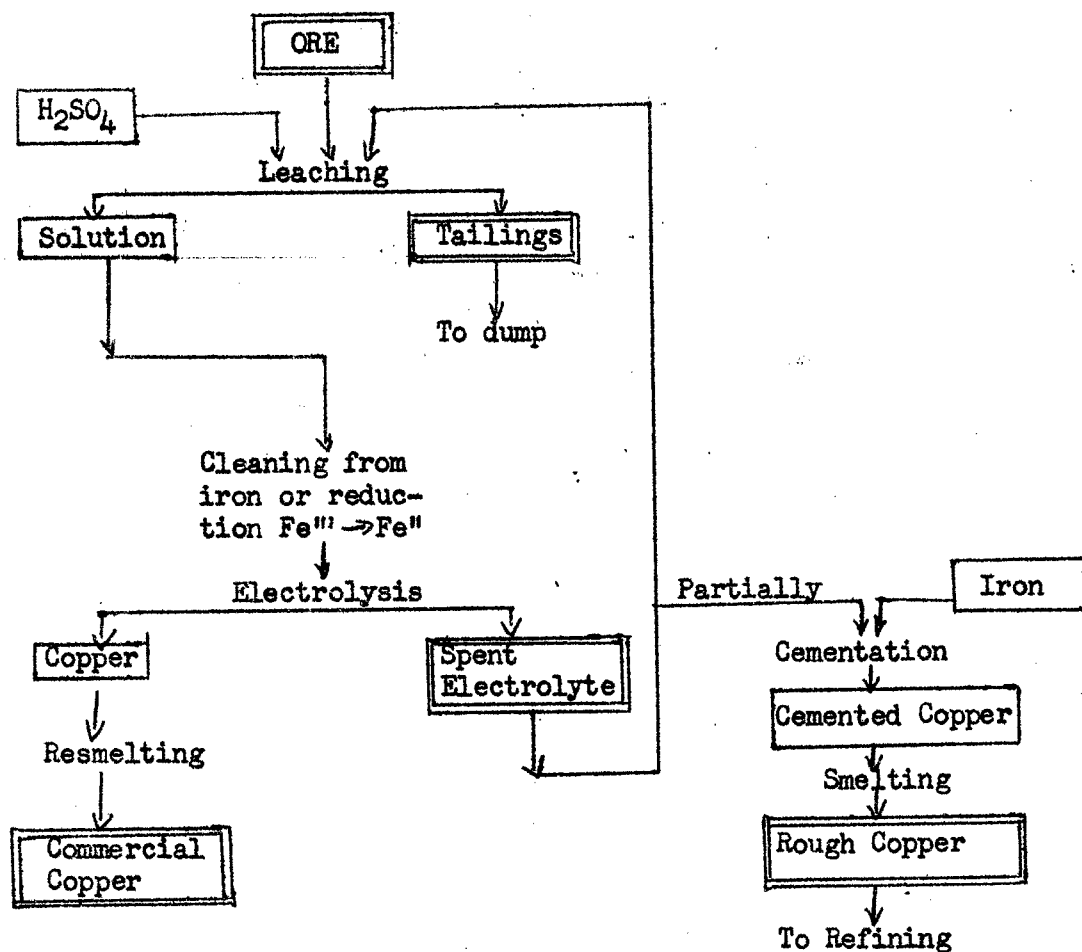


Figure 104. Diagram of Sulfuric Acid Method of Copper Extraction.